MATERIALS FOR THE ENERGY TRANSITION

CALORIC ENERGY CONVERSION MATERIALS

This publication forms part of the 'Materials for the Energy Transition' series. The Henry Royce Institute in collaboration with the Institute of Physics and the Institute for Manufacturing have convened the academic and industrial materials research communities to explore opportunities for materials to support the UK's net-zero by 2050 target.

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HENRY ROYCE INSTITUTE

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IfM MANAGEMENT TECHNOLOGY POLICY

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INTRODUCTION

The Challenge: Materials for the Energy Transition

Following release of the Committee on Climate Change (CCC) 2019 Report[1], the UK is committed to a new greenhouse gas emissions target: net-zero emissions by 2050.

The Executive Summary of the **2019 Committee on Climate Change Report** states:

> ***"Delivery must progress with far greater urgency.***
>
> - ***2040 is too late for the phase-out of petrol and diesel cars and vans, and current plans for delivering this are too vague.***
> - ***Over ten years after the Climate Change Act was passed, there is still no serious plan for decarbonising UK heating systems and no large-scale trials have begun for either heat pumps or hydrogen.***
> - ***Carbon capture (usage) and storage, which is crucial to the delivery of zero GHG emissions and strategically important to the UK economy, is yet to get started. While global progress has also been slow, there are now 43 large-scale projects operating or under development around the world, but none in the UK.***
> - ***However, falling costs for key technologies mean that the future will be different from the past: renewable power (e.g. solar, wind) is now as cheap as or cheaper than fossil fuels in most parts of the world."***

In response, the Henry Royce Institute (the Royce), in collaboration with the Institute of Physics (IOP), has engaged with academic and industrial materials research communities to explore solutions to the grand challenge of **"Materials for the Energy Transition"**. Through roadmapping workshops and associated community-led activities, technologies were identified where materials research can make a significant impact on greenhouse gas emissions.

The key drivers for this work have been (1) the pathways to net-zero emissions suggested in the CCC report, and (2) Royce-supported community workshops undertaken in 2019 to identify areas where investment in UK materials science can generate impact and contribute to the UK's energy transition. These included the "Atoms to Devices" workshop in Leeds (May 2019); the "Operando and In-Situ Characterisation of Energy Materials" workshop at the Diamond Light Source in Harwell (July 2019); and, the "Multi-Modal Characterisation of Energy Materials" workshop in Cambridge (November 2019).

As a consequence, the following four areas were identified where materials science is critical to enabling a step-change in greenhouse gas reduction:

1. Materials for photovoltaic systems
2. Materials for low-carbon methods of hydrogen generation
3. Materials for decarbonisation of heating and cooling

[1] Committee on Climate Change Report: Net-Zero, January 2019, https://www.theccc.org.uk/publication/net-zero-the-uks-contribution-to-stopping-global-warming/

I. Thermoelectric energy conversion materials
II. Caloric energy conversion materials

4. Materials for low loss electronics

MATERIALS ROADMAPS

In 2020, the Royce together with the respective research communities explored the various materials challenges, targets, and timescales required to support the achievement of net-zero greenhouse emissions by 2050 of the four research areas outlined above. The CCC report and the related materials community engagement emphasised that these four areas are components of a broader ecosystem of materials technologies which together contribute to the UK's goals to deliver net zero by 2050. These roadmaps form the basis for bringing scientific research communities, industry and government together to address immediate and long-term requirements for the development of a suite of energy materials to replace fossil fuel-based energy technologies. The Royce collaborated with the Institute of Physics (IOP) to set out the programme of work and ensure community-wide feedback and engagement. Skills and expertise from the Institute for Manufacturing (IfM) were commissioned to ensure a robust roadmapping methodology, throughout the series of online roadmapping workshops, and to support community discussions.

ROADMAP OBJECTIVES AND METHODOLOGY

The main objectives for the five materials roadmaps at the outset were as follows:

- To understand the current state-of-art for each topic
- To define the most significant technical challenges for each area that are providing barriers to impact on net zero targets
- To define the anticipated future challenges for each area in contributing to net zero targets
- To identify solutions to these challenges that can make step-changes in delivery of technologies to contribute to net zero targets
- To identify the desired performance targets of such solutions

The methodology adopted was based on wide-ranging engagement with research communities to define the roadmap objectives and expectations, to design and customise the strategic framework for the roadmapping, to develop questionnaires for the research communities involved, and to modify workshop process steps to ensure participation of the entire research community. The workshops brought together academic and industrial experts in the four respective technology areas and involved both offline and online data collection phases. The offline phases were used for data collection from individual participants and publicly available research sources, followed by data consolidation and, where necessary and appropriate, prioritisation. The online workshops were used for data review, analysis, and deeper exploration of essential issues. The quality and reliability of the process was maintained by a Steering Committee involving roadmapping facilitators and technical leads from each of the four research communities.

In total, 26 workshops sessions were held across the four technology areas between March 2020 and June 2020. These revealed several materials sub-topics of particular interest for contribution towards the net-zero targets, as well as highlighting important fundamental research and commercial technology enablers that need to be established. These outputs significantly aided research communities' understanding of the future direction of energy materials research, towards the achievement UK's net-zero emission targets by 2050.

Between March and June 2020, over 220 participants contributed to the creation of these five roadmaps from the UK academic and industrial materials communities. The outcomes are:

(1) an **executive summary** report, highlighting the main findings of the four roadmapping activities, published in July 2020;

(2) five **materials development roadmaps** towards net-zero emissions for 2050, published for research communities, funding bodies, government, policy-makers and industry leaders.

The five materials roadmaps generated are living documents, and Royce will engage with research communities regularly to review these documents and to develop further roadmaps as new materials systems and technologies emerge. We would like to thank all who have participated in these activities through the roadmapping workshops, interviews, surveys and research summaries.

Oversight of community activities was through the "Materials for the Energy Transition" Steering Group: Professor Neil Alford, (Imperial College London), Professor Manish Chhowalla (University of Cambridge), Professor Richard Curry (University of Manchester), Professor Edmund Linfield (University of Leeds)

Programme management, reporting, and community engagement was undertaken by Royce and IOP: Mia Belfield (Royce), Ellie Copeland (IOP), Anne Crean (IOP), Isobel Hogg (IOP), Judith Holcroft (Royce), David Knowles (Royce), Amy Nommeots-Nomm (Royce), Suman-Lata Sahonta (Royce), Philip Withers (Royce), Katharina Zeissler (Royce)

Roadmapping activities were coordinated by IfM: Nicky Athanassopoulou, Diana Khripko, Imoh Ilevbare, Arsalan Ghani, Andi Jones, Rob Munro

Technical oversight of roadmaps was undertaken by Oscar Cespedes (University of Leeds), Katharina Zeissler (University of Leeds), Oliver Fenwick (Queen Mary University of London), Robert Hoye (Imperial College London), Xavier Moya (University of Cambridge), Ifan Stephens (Imperial College London), Sam Stranks (University of Cambridge)

EXECUTIVE SUMMARY

17% of UK CO_2 emissions are from space heating and cooling as a result of burning natural gas and the use of volatile greenhouse gases as vapour-compression refrigerants. Reaching the 2050 net-zero carbon target will require contributions from energy-efficient refrigeration methods, and heat pumps based on solid refrigerants that can operate without gases. Caloric materials can provide a solution to these challenges. An efficiency goal greater than 50% -60% of Carnot for caloric cooling would be desirable, and would make the efficiency of caloric technologies competitive.

Experts in caloric technologies from around the UK were invited to discuss how caloric materials can impact the UK's target of net-zero greenhouse gas emissions by 2050. Engagement was through a series of workshops to develop research outlooks for the four main categories of caloric materials, in the context of their application for heating and cooling around room temperature, i.e. typical operation temperature ranges for refrigeration, air-conditioning, and heat pumps. These strategic research outlooks outline the R&D and the capabilities required to overcome the key challenges that are currently preventing the widespread application of caloric technologies. Although a % Carnot comparison of current device efficiency across all the calorics would be informative, most caloric system developments are as yet at an early stage. An issue that arose in a few of the roadmaps was a trusted measurement for e.g. solar cell efficiencies and this also applied to efficiencies of calorics.

Key materials R&D identified within the four categories of caloric materials include:

- Electrocalorics:
    - Improving electrical breakdown and thermal diffusivity in ferroelectric oxides.
    - Exploration of organic ferroelectrics, polymers (e.g. co- and terpolymers based on the vinylidene fluorides and possible nylon derivatives) and liquid crystals to find systems with large field-dependent spontaneous polarisations and tunable phase transitions near room temperature. .

- Magnetocalorics:
    - Improve the microstructure of mass-produced third generation magnetocalorics or explore composite magnetocaloric materials to reduce material fatigue and extend operating life.
    - Continue to explore novel cooling cycles that further reduce the quantity of permanent magnet required, such as the multicaloric cycle, asymmetric regeneration and hybrid gas / MCE cascade systems.

- Barocalorics:
    - Discovery of new materials with enhanced thermal response and temperature range of operation.
    - Understanding and reduction of hysteresis in materials with first-order phase transitions to reduce the driving pressure required.
    - Developing materials with increased thermal conductivity, which exhibit high entropy and temperature changes, and can work below 300 bar.

- Elastocalorics:
    - Discovery of new materials with enhanced thermal response and temperature range of operation.
    - Reduction of hysteresis, mechanical breakdown, and fatigue.
    - Developing precipitates for metals, and functional groups of polymers, to reduce driving stresses required.

Key device R&D were also identified, since device R&D must go hand-in-hand with materials R&D. These include:

- Develop efficient (>50% Carnot) devices using low cost caloric refrigerants.
- For those caloric cycles where an exchange fluid/gas is not incorporated, heat switches that are efficient, heat leak-free, fast, and have high on/off ratios, that can operate under high driving fields will need to be developed.
- Complete lifetime analysis (on accelerated timescales) that show robust properties in all components.
- Complete lifecycle analysis (LCA) to demonstrate the environmental benefits of each caloric technology. This will aid device and system developers to reduce environmental impact.
- In systems without an exchange fluid, understand how to thermally connect/couple the caloric material to the outside world/heat load without thermal bottlenecks.

On **required resources and capabilities**, there were important overlaps and commonalities across the four categories of caloric materials. These are:

- Funding for manpower in materials discovery, materials engineering and systems engineering, materials characterisation, computational materials modelling, and thermal modelling.
- Funding for state-of-the-art thermal testing facilities to develop caloric materials and devices.
- Academic-industrial partnerships with companies in manufacturing, air-conditioning, heat pumps, and refrigeration technologies.
- Standardisation of safety and performance metrics.
- Establishing a *Faraday Partnership,* or similar scheme, for exploration of zero-carbon cooling and heating. Establishing a cohesive forum for leading academics, companies, and critical players across the UK, under which all caloric materials strands and related research would be united, to address common challenges and share expertise.
- Schemes to enable access to synchrotron and neutron facilities for dedicated calorics research.

Successful breakthroughs in caloric technologies would not only permit decarbonisation of heating and cooling, but would enable the UK to become a global leader in net-zero heating and cooling technology markets, and contribute significantly to energy, environmental and job security. An area of importance is production scalability – those technologies that can harness existing production techniques (with minor modifications) would be in a stronger position to have an impact by 2050 than others. Indeed, this is one aspect of the larger (and more complex) cost question, but understandably the question of cost is hard to quantify for some of the early stage technologies under review. Nevertheless, an overview of cost barriers (critical materials, scale-up processes) or environmental barriers (use of lead or arsenic) that could stand in the way of wide scale adoption (and thus potential impact on net zero goals) will ultimately need to be addressed but it is outside the scope of a roadmap which focuses on material science and engineering.

BACKGROUND

Space heating and cooling of buildings contributes significantly to the UK's energy consumption[2] and to the UK's overall CO_2 emissions –totalling around 17% (BEIS, 2018a) – **Figure 1**. Prevailing technology is based on the combustion of fossil fuels, and vapour-compression refrigeration/heat pumping, which relies on repeated cycles of compressing, condensing, expanding and evaporating a volatile refrigerant fluid. Improvements in energy efficiency for vapour-compression systems are plateauing[3], and the refrigerants are environmentally harmful greenhouse gases based on hydrofluorocarbons (HFCs), which tend to have a high global warming potential (GWP)[4]. Lower GWP refrigerants have been developed [e.g. and hydrocarbons (HCs)] and are in use but are usually higher in toxicity, flammability, manufacturing costs, less efficient than current HFCs, or a combination of these[5]. Therefore, it is important to look into alternative technologies in order to achieve the

[2] Cooling of homes and working environments, food and vehicles represents about 20% of world energy consumption (Goetzler *et al.,* 2017 (US DoE)). Examples of how space heating (and cooling) contributes to energy consumption in the UK: space heating accounted for about 65% of domestic energy consumption between in 2018 (Energy Consumption in the UK BEIS, 2019); space heating accounted for 49% of the non-domestic building stock energy consumption (Business Energy Statistical Summary, BEIS, June 2018); up to 60% of electricity used in food retail and supermarkets is in refrigeration systems and 25-40% of total vehicle fuel consumption in food freight is accounted for by refrigeration (Energy demand and reduction opportunities in the UK food chain, Tassou et al., 2014).

[3] Refrigerator/Freezer Energy Efficiency Improvement in the APEC Region: Review of Experience and Best Practices APEC Energy Working Group, November 2018: https://www.apec.org/Publications/2018/12/Refrigerator-Freezer-Energy-Efficiency-Improvement-in-the-APEC-Region

[4] GWP is measured in equivalent CO_2 emissions for the lifecycle of the cooling system.

[5] F-Gas Support (2009) - Guidance on Minimising Greenhouse Gas Emissions from Refrigeration, Air-conditioning and Heat Pump Systems (https://www.fluorocarbons.org/wp-content/uploads/2009/06/rac_7_refrigerant_selection_new_feb_2009.pdf)

significant reductions in energy consumption and CO_2 emissions necessary for the UK Government's 2050 net-zero carbon target.

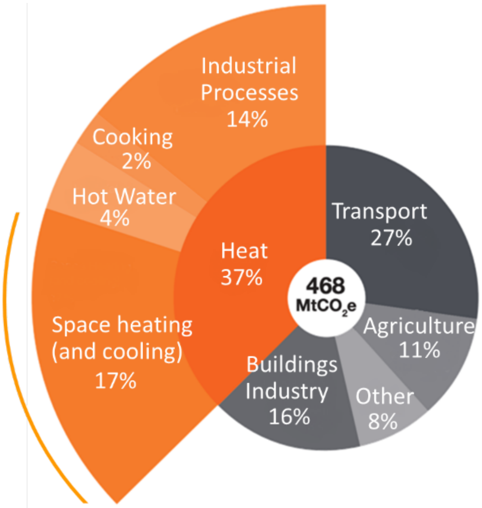

Figure 1. UK emissions in 2016. Space heating and cooling accounts for 17% of the overall CO_2 emissions, adapted from BEIS (2018a)

Caloric materials can provide a solution for zero-carbon heating and cooling. These materials are solid-state refrigerant alternatives that show reversible thermal changes, known as caloric effects, that are due to changes in applied driving fields (including magnetic fields, electric fields, stress and pressure) (Moya *et al*., 2014). While these materials are under intense study due to their potential for eliminating direct greenhouse emissions from heating and cooling applications, and great strides have been made in the last decade, critical challenges still need to be overcome to enable widespread commercial application and competitiveness with vapour-compression technologies. The criticality of the challenges associated with the development of caloric refrigeration, and the potential for huge gains (for the UK and globally[6,7]) if these challenges can be overcome, makes it important for the UK Government to promote and support R&D of this technology.

CALORIC MATERIALS, CALORIC EFFECTS, CALORIC COOLING AND HEATING CYCLES

Caloric materials undergo significant temperature changes ΔT when an external field – a magnetic field, electric field, stress, pressure – is applied to them (or withdrawn from them) adiabatically. Thus, caloric materials show reversible thermal changes, i.e. caloric effects that are due to changes in applied driving fields. These thermal changes are described not just in terms of adiabatic temperature change ΔT of the material, but also by isothermal entropy change ΔS and by isothermal heat Q, and they vary in intensity with the application of the field[8].

The research community has categorised caloric materials and named the caloric effects produced in these materials according to the nature of the driving field that produces them (Moya *et al*., 2014):

[6] Beyond the UK: there is great economic potential for technology breakthroughs in the global cooling and heating market; for example the global *domestic* refrigeration market was valued over £55 billion in 2017, expected to be over £100 billion by 2025 (https://www.grandviewresearch.com/press-release/global-household-refrigerators-freezers-market).

[7] According to Cui *et al.* (2015), and in the context of the U.S., "the goal… [is to develop] operational caloric cooling devices that, ultimately, realises a potential for 20-30% drop in U.S. energy needs for cooling"

[8] In conventional caloric materials, and increase in the driving field leads to $\Delta T>0$, $\Delta S<0$ and $Q<0$, while converse is the case for inverse caloric materials (Moya *et al*., 2014).

- Magnetocaloric materials (or simply, magnetocalorics, MCs) show reversible thermal changes (i.e. magnetocaloric effects, MCEs) in response to changes of applied magnetic field
- Electrocalorics (ECs) show reversible thermal changes (i.e. electrocaloric effects, ECEs) in response to changes in applied electric field
- Elastocalorics (eCs) show reversible thermal changes (i.e. elastocaloric effects, eCEs) in response to changes in uniaxial stress, and
- Barocalorics (BCs) show reversible thermal changes (i.e. barocaloric effects, BCEs), in response to changes in hydrostatic pressure.

Elastocalorics and barocalorics are together referred to as mechanocalorics (Moya *et al.*, 2014) since, uniaxial stress and hydrostatic pressure are both mechanical stresses. Multicaloric materials are those that can develop thermal changes in response to more than one type of driving field.

Using the caloric effect for refrigeration and heat pumping purposes requires a thermodynamic cycle to be applied and, in this regard, all caloric technologies have similar principles of operation. A simple illustration of the caloric cooling/heating cycle is provided by Takeuchi & Sandeman (2015) is shown in **Figure 2**. Consider a caloric material with original temperature T_1. Adiabatic application of a driving field causes the caloric effect – a temperature increase to T_2 – in the caloric material, from which heat can then be extracted (for heat pumping purposes), or dumped, thus reducing the temperature of the caloric material to T_3. Adiabatic removal of the driving field further causes a caloric effect, i.e. further reduction of the caloric material's temperature to T_4 – low enough to enable heat absorption from a space requiring cooling (e.g. inside a refrigerator) into the caloric material. This absorption of heat causes an increase in the temperature of the caloric material back to its original temperature state T_1.

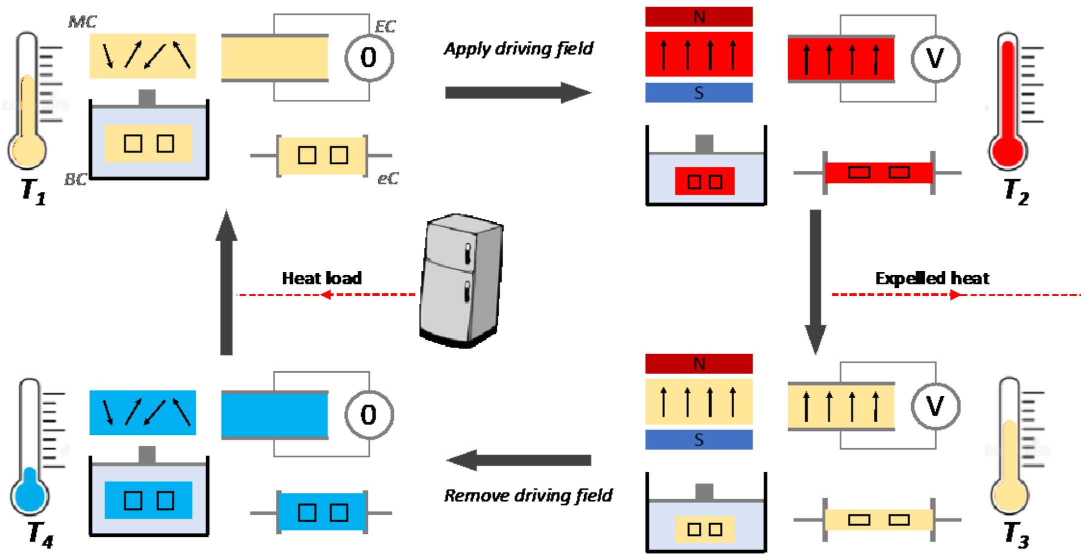

Figure 2. Caloric material cooling cycle using magnetic, electric, pressure, or stress fields to reversibly change temperature (adapted from Takeuchi & Sandeman (2015) and Crossley et al. (2015)).

In vapour compression technology, the refrigerant is also the circulating fluid and heat transfer medium. In calorics (which are solid refrigerants), the system usually requires a fluid and a fluid circulatory system to serve as the heat transfer medium between the solid refrigerant and the heated/cooled spaces.

A number of cooling cycles can be considered. The basic cycle is illustrated in **Figure 2**. Regenerative cycles involve the circulation of a heat transfer fluid to carry heat to and from the caloric material, and to develop a temperature gradient along both the material and the fluid, thereby increasing the working temperature span of the device. Active regeneration is attractive because it can be used to create large operating spans (e.g. Stirling Cycle regeneration). Regenerative cycles have been heavily studied in recent decades and are an active area of research in calorics (Takeuchi & Sandeman, 2015), being the only cycle so far to deliver high-performing caloric devices. The cascade cycle has been reviewed as an alternative. Here, the caloric material is built as a cascade where segments of the caloric material are coupled through thermal diodes. This cycle requires the use of thermal switches between cascade elements (Hess *et al.,* 2019). It is important to note that heat switches and thermal diodes are quite different and are used in substantially different cooling cycles. The thermal diode is referring to the work by Hess *et al.* (reference Hess *et al.,* 2019), and it is a check valve for vapour i.e. vapour can pass through it in one direction only. In Hess's system, a cascade of magnetocaloric materials is being used to progressively pressurise gas i.e. at step N, the MC is magnetised and warms up, causing gaseous evaporation and this gas passes through a check valve to the next MC chamber in the cascade at a slightly higher pressure. At the end of the cascade the now pressurized gas is rapidly expanded to provide cooling. The gas transports heat (latent heat) and provides the cooling (like in a gas compressor), not the magnetocaloric material. The heat switch (as specified earlier in the document), is more appropriate for a system based around a fully solid state system, where each caloric material is separated by a heat switch. By energising each of the caloric materials in the correct phase, and assuming there is sufficient thermal response, heat can be pumped progressively (by conduction – so relatively slowly) from cold to hot. The heat switch required for this type of caloric device is significantly more complicated than Hess's thermal diode. Although mechanical versions have been tried (particularly in the field of ECs), a solid state version with adequate properties does not yet exist, although it has been discussed in the literature that thermoelectrics might operate sufficiently efficiently (as they are in low span mode) to act like a heat switch between MC elements.

NEED FOR ACTION

Magnetocalorics (MCs) and electrocalorics (ECs) have been at the forefront of research into caloric cooling. Well-engineered regenerative magnetic cooling cycles can support operating temperature spans of up to ~100K[9] and regenerative cooling cycles have been reported to deliver device efficiencies of up to 60 % of Carnot[10]. Third generation low-cost and high-performance magnetocaloric alloys have been industrially developed and these successfully deployed in regenerative cooling cycles[11]. The challenge is to create devices with the specific features needed for, and at a cost appropriate to, mass-market applications, whilst demonstrating a 5-10 year device lifetime. Electrocalorics have been actively investigated since the mid-2000s and typically require high electric fields that can be applied without breakdown using relatively thin samples in order to achieve thermal changes that can be exploited in prototypes.
Recently more attention has been given to mechanocalorics[12], since mechanical stress is easy to generate, and large mechanocaloric effects have been observed at moderate applied stresses[13]. Nevertheless, research continues in all four caloric effects and this report presents a strategic research outlook based on the input of leading UK experts in the area of caloric materials, to guide

[9] "Performance investigation of a high-field active magnetic regenerator", Teyber R. et. al.,, Applied Energy, Volume 236, 15 February 2019, Pages 426-436

[10] Chaudron, J. B., Muller, C., Hittinger, M., Risser, M., & Lionte, S. (2018). Performance measurements on a large-scale magnetocaloric cooling application at room temperature. In *Proceedings of Thermag VIII, 8th IIR/IIF International Conference on Caloric Cooling*. International Institute of Refrigeration.

[11] Jacobs et al. (Astronautics) reported a maximum temperature span of 18 K in a large-scale rotary magnetic refrigerator prototype that uses La-Fe-Si alloys: http://dx.doi.org/10.1016/j.ijrefrig.2013.09.025

[12]Section 2.2 of this report presents the challenges associated with the caloric effects in more detail.

[13]Moya 2020 https://patents.google.com/patent/WO2018069506A1/en

UK investment for R&D to maximise the potential of caloric technologies to contribute to the achievement of the UK's 2050 net-zero emissions goals.

WORKSHOPS ON THE DECARBONISATION OF HEATING AND COOLING USING CALORICS

As part of a wider series of workshops hosted by the Henry Royce Institute, focused on enabling the development and adoption of materials science to contribute to the UK's net-zero emissions target, workshops were carried out to identify a strategic research outlook for the UK in caloric technologies. The workshops brought together thirteen leading UK experts in calorics. Appendix A contains the list of participants along with a record of the workshop proceedings.

The workshop originally set out to address the following issues:

(i) identifying which caloric material systems show the most promise for viable energy-saving applications towards net-zero emissions by 2050,

(ii) identifying the key standards and metrics for comparing performance of materials and devices, and how these metrics can be combined to establish a single figure of merit for materials and devices,

(iii) establishing performance levels of current materials, and what may be achieved by 2025, 2035 and 2050,

(iv) understanding the materials challenges that limit deployment of calorics-based technologies, and

(v) (v) understanding what (and how) improvements can be made in advanced characterisation of caloric materials and devices.

Given that there are several still unresolved challenges across the four caloric materials categories, and across materials within these categories, the research community agreed to refocus workshop discussions more broadly on the four categories (i.e. MC, EC, eC and BC) instead of individual materials and material systems. This way, rather than attempting to identify individual caloric materials that 'show most promise', critical unresolved challenges across and within the four materials categories (which, if resolved would make significant positive impact on the adoption of caloric technologies) were discussed. It was agreed that addressing issues from this more integrated perspective would, at this stage, be more beneficial[14].

Therefore, each category of caloric material (and associated caloric effects) was examined, focusing on near-room-temperature applications (i.e. -50 to +50 °C) in answering the following questions:

- What is the key challenge (i.e. the Achilles' heel) limiting deployment in applications?
- What R&D advances can we suggest to overcome this challenge?

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[14] Other reasons were expressed by the caloric materials community why the revised approach would be more appropriate:

i. Despite knowledge of caloric effects for many decades, intensive research into this area has only recently accelerated, and the field is still relatively immature. An illustration of this can be found in the characterisation of magnetocalorics and electrocalorics, the two most mature of the four categories, as being at TRL 3-4 and TRL 1-2 respectively by the US DoE (Goetzler *et al.,* 2017).

ii. There is significant difficulty in standardising conditions for measuring material and device performance levels, and therefore future targets for performance, resulting in difficulty in defining a single figure of merit (FOM) for materials (and devices), which would enable objective comparisons. This may be illustrated by Griffith *et al*. (2018) attempt to define an FOM for magnetocaloric materials. Authors noted that the complexity of the materials and the need to consider multiple properties and parameters could easily lead to misinterpretations.

iii. Materials and device (i.e. application) R&D must be done concurrently in order to achieve the breakthroughs required, and therefore integrated thinking (and therefore a broad perspective on the calorics field) is necessary. According to Takeuchi & Sandeman (2015), "… key innovations will likely come from the intersection of materials development and systems design efforts, principally through maximising caloric effects and heat-exchange properties" p54.

- What resources and capabilities, including funding and facilities, do we think are needed to enable the R&D advances we suggest?

The following sections of this report present the following:
- A snapshot of the state of art in caloric materials (for near-room-temperature applications) and the general challenges associated with calorics and devices
- Challenges associated with each category of caloric materials, the key weaknesses associated with each one, and a strategic research outlook in response to the key weaknesses or challenges for each category. This part provides answers to the questions posed for the workshop, and the answers are based on deliberation and consensus among the experts consulted in this study.

STATE OF ART OF CALORIC MATERIALS AND DEVICES FOR NEAR-ROOM-TEMPERATURE APPLICATIONS

Here we highlight some of the recent advances made in caloric technologies and also present some of the generic challenges associated with calorics (as identified from literature). We have not attempted to provide a detailed picture of the state of art, but have drawn on published papers that have successfully done this[15].

Magnetocalorics

It is worth noting that magnetocalorics are the most well-developed of the caloric technologies (Moya & Mathur, 2020). Regenerative cooling cycles have achieved large cooling powers, operating with a < 1 T field over 20K operating span (Kitanovski *et al.*,2016, Chaudron *et al*., 2018), albeit using first-generation Gadolinium alloys. However, over the last 10 years there has been an increasing use of third generation low-cost Fe based alloys in prototypes with $La(FeSi)_{13}$ alloys in particular. A proof of concept machine using $La(FeSi)_{13}$– based alloys has been developed to meet requirements of a naval supplemental electronics cooler, having a maximum temperature span of 18 K and a maximum power of 3 15 kW (Jacobs *et al.* 2014)[16]. Separately, a research team from the Technical University of Denmark (EnovHeat project) published the demonstration of a prototype magnetocaloric heat pump (based on $La(FeSi)_{13}$ alloy MC material) capable of maintaining a Danish family home at 20 °C using around 16kWh/m^2, typical for northern European homes during winter (Johra *et al*., 2018). Currently there are two standards for magnetic cooling – one officially published, and one approved but awaiting final publication: DIN_91373[17] and DIN_SPEC_91373-2[18].

Electrocalorics

Electrocaloric materials are primarily ceramics and polymers and these tend to be low cost. Electrocalorics require electric fields to drive these materials to produce the ECE. The active materials in most prototype EC devices include PST (lead scandium tantalite, a ceramic), $BaTiO_3$ (barium titanate, a ceramic) , PMN-PT (lead magnesium niobate-lead titanate, a ceramic) and PVDF (poly(vinylidene fluoride-trifluoroethylene), a polymer). Given the generic inverse relationship

[15] Review paper from Moya and Mathur, *Science* **370**, 797 (2020). Greco *et al.*, (2019) presented a detailed account of advances in caloric cooling processes providing an overview of all refrigerator and heat pump prototypes based on caloric effects for room temperature applications with an emphasis on prototypes developed after 2010. It should be noted that Yu *et al.*, (2010), covered similar ground (but limited to magnetocalorics) for prototypes earlier than 2010.

[16] A maximum temperature span of 42K was reported by Kitanovski *et al.* (2016) in a 2013 prototype device which used Gd and Gd alloys as MC material.

[17] DIN Deutsches Institut für Normung e. V., 'Magnetocalorics – Terminology' DIN SPEC 91373:2018-06' (2018)

[18] DIN Deutsches Institut für Normung e. V., 'Measurement of magnetocaloric properties' DIN SPEC 91373-2 (2020)

between breakdown field and material thickness, thin film formats of these materials can be driven harder[19] than the bulk formats to produce larger EC effects (Moya *et al.,* 2014). However, thin films, generally have inadequate volume to deliver useful cooling/heating capacity for e.g. HVAC applications with their main potential lying in on-chip cooling of (and energy recovery from) semiconductor devices. Assembling thin films in the form of a multilayer capacitor (MLC) provides a more viable working material. Temperature spans in the region of 6 K have been reported by Gu *et al.,* (2013) in a prototype using irradiated PVDF 62/38 co-polymer (building on the work of Lu *et al.,* (2010) in multilayer configuration as the working material). Nair *et al*. (2019) demonstrated high-quality MLCs made of several PST layers ($PbSc_{0.5}Ta_{0.5}O_3$) that display large electrocaloric effects showing ΔT of about 5.5K near room temperature (Moya and Mathur (2020)).

Elastocalorics

The active material in prototype devices includes Ni-Ti plates and Ni-Ti wires. It has been shown that shape-memory alloys (SMA) of Ni-Ti show the largest eC effects (Moya e*t al.,* 2014). Engelbrecht *et al.* (2017) reported experimental results for a prototype device made of Ni-Ti alloys in the form of parallel plates (0.35 mm thickness) which achieved a maximum temperature span of 19.9 K[20].

Barocalorics

Barocalorics are at the earliest stage of research of the four caloric effect technologies, but growing rapidly. Stern-Taulats *et al.* (2018) presented initial designs of a barocaloric cooler that operates at room temperature under small applied pressures. Large BC effects have been observed near room temperature in magnetocaloric materials, such as the super-elastic magnetic Ni-Mn-In alloy (Mañosa *et al.,* 2010) and inorganic materials such ammonium sulphate (Lloveras *et al.,* 2015). Lloveras *et al.,* (2019) reported plastic crystals of neopentylglycol $(CH_3)_2C(CH_2OH)_2$ as showing promisingly large pressure-driven thermal changes near room temperature[21].

Common challenges across caloric materials

Despite the advancements in calorics (some of which have been described in the preceding paragraphs), there are certain challenges that are common across caloric materials, which need to be addressed in order to deliver transformational caloric heating and cooling that can achieve market acceptance. These include:

- **Driving fields:** All caloric based applications would be improved if the fields required to drive the materials in order to produce caloric effects were reduced (Cui *et al*., 2015). How the materials are driven is an important issue. For example, how costly is the driving field? How efficiently is that driving field delivered?
- **Energy Recovery:** Efficient caloric devices require energy recovery – i.e. being able to reuse the energy relinquished when removing the applied field to drive the application of the field in the next cycle. An inability to efficiently deliver energy recovery will severely hinders the efficiency of most caloric devices. Energy recovery has been implemented in full in magnetocalorics, with some success in electrocalorics.
- **Fatigue life (and cycle life):** one of the key concerns is the fatigue life of caloric materials, especially if one considers that residential equipment such as refrigerators can run several

[19] A ΔT of 20K @ 160MV/m – a very high field intensity – was reported in a thin film of high energy electron irradiated P(VDF-TrFE) 68/32 copolymer by Lu e*t al.* (2010).

[20] In the same paper, Engelbrecht *et al.* (2017) reported results for a second prototype device, also made of Ni-Ti alloys in the form of parallel plates (0.2mm thickness) with a maximum temperature span of 17.6K.

[21] Further to this, Moya *et al.* (2020) have now shown that other organic materials (including plastic crystals, liquid crystals and hybrid organic-inorganic materials) can produce giant barocaloric effects.

millions of cooling cycles over their lifetime. Therefore, there is a need to demonstrate that caloric materials can be driven back and forth through millions of cooling/heating cycles without mechanical or chemical breakdown (Takeuchi & Sandeman, 2015).

- **Refrigeration cycle losses:** Continue the exploration of innovative cycles that can deliver the desired temperature span under real-world operating conditions and which minimise losses. If a heat transfer fluid is used, the contact between heat transfer fluid and the caloric material can introduce corrosion. Some types of cycle require the use of thermal heat switches which are still under development.
- Perform **lifecycle analysis** for all caloric systems to assess their true environmental impact from pre-production to end-of-life.
- **All the caloric refrigerant materials are solid**, so heat needs to move rapidly by conduction from the solid refrigerant. In many caloric materials and certain types of purely conductive caloric cycles this can represent a thermal bottleneck that limits the power density of a device (operating frequency), the maximisation of which is critical for ensuring low-cost and compact cooling devices.

KEY CHALLENGES AND STRATEGIC RESEARCH OUTLOOKS FOR CALORIC TECHNOLOGIES

In this section, we present the strengths and weaknesses (or challenges) associated with each category of calorics and highlight the most critical challenge. A strategic research outlook for the caloric technology is then provided, suggesting the main materials and device R&D advances and resource/capability needs required to overcome the critical challenge.

Magnetocalorics

Magnetocalorics prototypes are well ahead of the others in terms of performance (Kitanovski *et al.* 2016). With the ability to mass-produce high performance third generation alloys and useful device architectures proven, this technology is the most mature.

Strengths of magnetocalorics

Magnetocalorics are very energy-efficient materials, exhibiting minimal hysteresis (once optimised) and reversible phase transitions. Devices using first generation magnetocaloric alloys (based on Gadolinium) have achieved high performance (Chaudron 2018 reported 60% of Carnot), this being possible because full energy recovery can be successfully implemented with magnetocaloric cooling cycles and the driving field (produced by relatively inexpensive permanent magnets) incurs no direct energy cost.

Third generation magnetocaloric alloys can be mass produced in a variety of ways, and these newer alloys show stronger response to magnetic field (with the same thermal response) compared to Gadolinium, contain no critical raw materials, do not use any heavy rare earths, and these alloys, once configured into regenerators, have been shown to endure for more than 5,000,000 cycles[22] (at least a few months of operation). Systems based upon third generation alloys are still in development, but, already it has been shown that such systems are largely recyclable at end-of-life (Walton, 2015), and life-cycle analysis already shows that the environmental impact of MC devices during pre-production and production is already comparable to that of a gas compressor Luglietti *et al.* (2017).

[22] LaFe Si-Based magnetocaloric material analysis: cycle endurance and thermal performance results, Sergiu Lionte *et al.*, International Journal of Refrigeration 124 (2021) 43–51

Weaknesses of magnetocalorics

The following weaknesses of MCs were highlighted:

- To achieve cost-effective mass-production of high-efficiency magnetic cooling, devices using third generation magnetocaloric alloys are required. Third generation alloys undergo first-order 'like' magnetic phase transitions and with correct doping the hysteresis normally associated with a complete first-order transitions can be eliminated (Scheibel *et al.* 2018), but sub-optimal microstructure in mass-produced material can still generate residual fatigue and cracking. Adjusting the microstructure to minimize fatigue is critical to achieving the desired material longevity and production yield. As an alternative, further work on MC composites is an option, although the here the challenge is to maximise the density of the MC material in the composite.
- From a cost perspective it remains desirable to be efficient in the use of permanent magnet through the development of novel cooling cycles.

These weaknesses were translated into research challenges for MCs:

- ***Mass-produced third generation alloys either needs to optimise the microstructure to mitigate the strain built up, or be incorporated into a composite structure that can relax the strain.***
- ***To further reduce costs, it would be advantageous to continue the development of novel MC cooling cycles that reduce the quantity of permanent magnet required.***

The strategic research outlook for MC (presented in **Figure 3**) was created via experts' deliberations in response to these challenges.

Proposed MC research and development initiatives

The following is an outline of the R&D initiatives included in the MC strategic research outlook shown in **Figure 3**.

Research and development

- Materials R&D
  - To reduce material fatigue either refine the microstructure of mass-produced third generation MC alloys or explore composite MC materials.
  - Explore the use of hybrid materials to take advantage of thermal hysteresis in novel (e.g. muticaloric) MC cooling cycles.
  - Support wider research into novel lower-cost permanent magnets (e.g. ferrite materials, which are cheaper but offer lower absolute field than rare-earth magnets)[23].
- System/Device R&D
  - Reach >50% Carnot efficiency using magnetocaloric materials based around low cost third generation MC materials
  - For Cascade cycles, develop heat switches that are heat leak-free, fast, and have high on/off ratios
  - Perform lifetime analysis on accelerated timescales to show robust properties in all components for at least 5 years, and for some applications up to 10 years.
  - Continue to investigate novel refrigeration cycles that reduce the quantity of permanent magnets used in devices

[23] Research into magnets is not considered caloric research, but there are direct implications for magnetocalorics if cheaper or stronger magnets can be developed. Breakthroughs in this area would also solve crucial problems faced by other allied (zero-carbon) industries, e.g. hydroelectric, wind and tidal energy.

Most critical weakness	**- Demonstrating 5-10 year life time of third generation magnetocaloric materials**	**Corresponding research challenges**	**- How do we mitigate the strain built up in the microstructure of third generation magnetocaloric alloys?**

	Short term (Present - 2025)	Medium term (2025 - 2030)	Long term (2030 - 2040)

Material R&D

- Magnetocaloric materials discovery (theoretical materials discovery preferred in the short term)
  Existing families of materials have some combination of challenges, e.g. fatigue/corrosion, measurable performance in small magnetic fields
- Work wirth materials producers to refine microstucutre of current mass produced MC materials.
- Explore alternative composite magnetocaloric materials for reducing strain/fatigue and corrosion
- Automate manufacturing processes for magnetocaloric components.
- Explore hybrid materials for use in multicaloric cooling cycles.
- Support R&D into materials for heat switches, and guide their development for potential application in magntocaloric cooling.
- Support R&D into alternative permanent magnet materials, that may help to lower long term cost.

System/ Device R&D

- Delivery >50% energy efficiency with third generation alloys
- Develop systems based on final use application specifications
- Scale-up of devices
- Lifetime testing (on accelerated timescales) that show robust properties in all components for 5 - 10 years.
- Continue to develop novel cooling cycles that reduce the cost of magnetic cooling to drive long-term price

Required resources and capabilities

- Access to more Synchrotron and Neutron facilities - maybe to have priority access
- Funding for systems engineering, characterisation, computational materials modelling and thermal modelling
- Funding for the development of bespoke experimental systems and equipment to measure certain parameters within prototype environment.
  This is not trivial and requires a multi-disciplinary development of components, sensors etc.
- Funding for networks - perhaps with EPSRC support
  (see the following EPSRC-relevant links: https://epsrc.ukri.org/funding/calls/decarbonising-heating-and-cooling/ and https://epsrc.ukri.org/newsevents/news/decarbonising-heating-and-cooling-for-net-zero-survey-of-needs/)

Consequences of successfully overcoming the key weakness	Sufficiently near-term delivery of enhanced efficiency cooling / heating devices to actually have an impact on 2050 climite mitigation goals		
Key assumptions	Key assumption: The high performance achieved with first generation magnetocalorics can be mapped to third generation materials and the associated microstructural issues can be solved relatively quickly.	Potential risks?	Full material longevity is not achieved, limiting addressble market and potential climate change impact.

Figure 3. Strategic research outlook for Magnetocalorics

Electrocalorics

Four classes of electrocaloric materials were recognised and therefore strengths and weaknesses were discussed along these lines. The four classes of ECs are all ferroelectrics (Whatmore *et al.* 2021):

- Ferroelectric oxides, these are mostly based on the perovskite crystal structure, but others are also possible (e.g. tungsten bronzes). They can be categorised broadly as either lead-containing (e.g. lead zirconate titanate (PZT), lead magnesium niobite-lead titanate solid solutions (PMN-PT), and lead scandium tantalate (PST)) or lead-free (e.g. barium strontium titanate (BST), and bismuth sodium titanate (BNT)).
- Ferroelectric polymers, e.g. poly(vinylidene difluoride) (PVDF) and the copolymeric material poly(vinylidene fluoride- co -trifluoroethyene) [P(VDF-TrFE)].
- Organic and molecular ferroelectrics, e.g. TTF-QBRCl$_3$ [tetrathiafulvalene (TTF)-2-bromo-3,5,6-trichloro-p-benzoquinone (QBrCl$_3$)].
- Ferroelectric liquid crystals, e.g. SCE13 (which is commercially available).

Strengths of Electrocalorics

Ferroelectric oxides exhibit measured ΔT values of about 5-10 K. These materials have moderate thermal diffusivities (D_T) and they are easy to make and modify. An industry already exists for multilayer chip capacitors (MLCCs) and multilayer piezoelectric actuators (MLPAs) in forms which are close to what would be needed for future EC cooling applications.

Ferroelectric polymers promise electrocaloric effects larger than those observed in EC oxides. Higher values of ΔT (e.g. ΔT of 20 K at 160 MV/m – a very high field intensity) have been reported in P(VDF-TrFE) 68/32 copolymers[24] than in typical oxides because very high fields can be sustained by these polymers[25]. They have very high resistivities and breakdown fields. The polymers are flexible, non-brittle and regularly manufactured into multilayer structures with interdigitated electrodes (this is already executed on a large scale in the capacitor industry with a range of polymer films, including polyester and PTFE, which are closely-related to the PVDF-TrFE family) and the raw materials used to make the materials are inherently low-cost.

Organic and molecular ferroelectrics are novel and currently in basic research, and they promise electrocaloric effects larger than those observed in EC oxides. Some of the best pyroelectric materials for pyroelectric infra-red detectors are based upon the hydrogen-bonded triglycine sulphate (TGS) family of ferroelectrics, which are related to this newer class of caloric materials. Their EC effects have been explored previously, but only at very low applied fields. Liquid crystal systems have the additional advantage of tuneable functional properties.

Weaknesses of Electrocalorics

Ferroelectric oxides are known to have ΔTs that are within the range of what is marginally useful[26]. However, high electric fields are required to achieve these ΔT values, which means that thin films/layers in the 1-2 micron range and, ultimately, the fabrication of multilayer capacitors (MLCs)

[24] See Lu *et al.* (2010).
[25] During the workshops, experts debated this reported ΔT of 20K, and it was unclear whether it was taken from direct or measurements or indirect extrapolation.
[26] Although this weakness was identified and agreed among experts during workshop discussions, electrocaloric prototypes are starting to show good performance. An example of that is seen in Nair *et al.* (2019) who demonstrated large EC effects (ΔT of 5.5K) by an electric field of 29 MV/m in a ferroelectric oxide (which is relatively low in comparison to driving fields of 100 MV/m for a measured ΔT of 5K in a polymer as reported by Gu *et al.* (2013)).

are necessary. Significant materials and manufacturing engineering will be required to make structures for EC applications (e.g. to allow penetration of regenerator fluids). In addition, survivability and lifetime of MLC EC structures at the necessary fields up to 10^{12} cycles is currently unknown.

Ferroelectric polymers such as PVDF-TrFE copolymers have low thermal diffusivities at values of approximately 0.1 µs (however, this can be mitigated to some extent by the use of interdigitated metal electrodes[27]). They are currently not made in large quantities and are consequently quite expensive to buy. Similar to ferroelectric oxides, significant materials and manufacturing engineering will be required to make suitable structures for EC applications. Similar to oxides, survivability and lifetime of MLC EC structures at the necessary fields up to 10^{12} cycles is unknown.

Organic and molecular ferroelectrics are promising materials but tend to suffer from electrical leakage and inhomogeneous caloric response, respectively. Most molecular ferroelectrics have very low spontaneous polarisations (e.g. molecular crystals are becoming competitive in terms of spontaneous polarisation, with record-holding croconic acid derivatives reaching 20 $\mu C/cm^2$ above room temperature). These materials are water/organic solvent soluble and mechanically soft, and thus difficult to use in an industrial context. They are likely to have rather low thermal diffusivities; for TGS (triglycine sulphate), D_T is around 0.2 µs, double the value of the ferroelectric polymers, but much lower than the oxides. The electrocaloric effect is small in liquid crystal systems (since higher spontaneous polarisation is necessary) but they are worth pursuing because a liquid EC system gives automatic energy recovery in comparison to a solid system.

It was agreed that the most critical weakness across ECs is that the ΔT currently achievable is modest and the electric fields that are required to achieve a wider range of ΔT are quite high[28].

This key weakness was translated into the following research challenges for ECs:
- ***Might there be materials (new or existing) out there that have much larger ΔTs at lower driving fields?*** [29]
- ***Can we make (i.e. processing and synthesis) the materials in the format required (e.g. for cycling) to sustain the fields needed?***

The strategic research outlook for EC (presented in **Figure 4**) was created via discussions in response to these challenges. This research outlook presents R&D initiatives according to the four classes of EC materials over time.

Proposed EC R&D initiatives and resource/capability needs

The following is an outline of the R&D initiatives and the key resources required as agreed during the workshop (shown over time in the EC strategic research outlook - **Figure 4**).

- Materials R&D: presented here by class of EC material
    - Ferroelectric oxides:
        - Investigate low-cost, low-environmental-impact materials with high coefficient of performance (CoP)

[27] Metallic electrodes can help transfer heat between thermally insulating EC layers (Kar-Narayan & Mathur, 2009).
[28] However, as mentioned in the review on current state of the art note that Nair *et al.,* (2019) demonstrated large EC effects (ΔT of 5.5K) by an electric field of 29 MV/m in a ferroelectric oxide (which is relatively low in comparison to driving fields of 100 MV/m for a measured ΔT of 5K in a polymer as reported by Gu *et al.,* (2013)).
[29] While addressing this challenge, it is also important to keep in view the need for higher thermal conductivity/diffusivity.

        - Explore/develop and demonstrate MLC-type structures that will permit regenerator penetration (average layer thickness in the sub-5 micron range, designed for good thermal coupling to regeneration fluids)
        - Improved electrical breakdown, and improved thermal diffusivity

    - Ferroelectric polymers:
        - Explore new ferroelectric polymers to obtain high, field-dependent spontaneous polarisations and ΔT's. These may be based on known systems, such as the co- and terpolymers of vinylidene fluoride or derivatives of the ferroelectric nylons with novel side-chains, or entirely new systems such as polymeric liquid crystals
    - Organic and molecular ferroelectrics
        - Basic research into molecular ferroelectrics (e.g. to reduce leakage) and to explore different schemes for ferroelectricity in organics
        - Research to improve processing (e.g. in thin films and composites) and efficiencies
        - Identification of strategies to improve the heat transfer limitation
    - Ferroelectric liquid crystals
        - Basic research into maximising spontaneous polarisation, polar nematics, hybrid systems and potential of tunability of phase transitions
        - Development of a family of polar nematic liquid crystals

- System/Device R&D
    - Research into electronics to drive the systems and materials, e.g. the use of inductive circuitry and switching techniques to recycle the charge
    - Understanding and demonstrating to transfer heat out of the EC material, and what materials are compatible electrically and thermodynamically; identifying what regenerator fluids are appropriate for EC and understanding how to couple the regenerator to the caloric material
    - Identifying other fabrication technologies for oxides other than the established processes used for capacitors

Required resources and capabilities
There are key resource and capability requirements that cut across the caloric technologies (as presented in the section discussing Cross-cutting resource and capability needs). However, resources/capabilities specific to EC were identified:

- Electronics to drive the systems, i.e. electronic engineers are required to work on the electronics and drive the system and materials
- Leveraging on capacitor technologies being developed for electric cars to further the advancement of MLCs
- Industry partnerships with ceramic capacitor manufacturers for demonstration of MLC structures, which require ceramic processing and electrode development
- Need to develop UK capability for producing high-quality MLCs

ECs appear to have the advantage (over the other caloric technologies) that they are driven very simply using a voltage, and electrical control of any device may be taken as a given. Successfully overcoming the challenges associated with EC would require (as with the other caloric technologies) a collaborative system among leading academics and critical industry players across the UK.

Most critical weakness(es)	Current ΔT are just in the range of marginally useful; The fields that are required to achieve a wider range of ΔT are quite high	Corresponding research question(s)	- Might there be [new] materials out there that have much larger deltaTs at lower driving fields? - Can we make (i.e. processing and synthesis of) the materials in the format required (e.g for cycling, to sustain fields needed)?

		Short term (Present - 2030)	Medium term (2030 - 2035)	Long term (2035 -2050)
Material R&D	Ferroelectric oxides	Investigate low cost low environmental impact materials with high CoP		
		Explore/develop MLC-type structures that will permit regenerator penetration	Different processing methods, e.g. solution spray; spray pyrolysis, ideally at ambient temperature and pressure	
		Explore/develop improved thermal diffusivity structures		
		Improve electrical breakdown	Demonstration of MLC structures with significant volume and average layer thickness in the sub-5 micron range, designed for good thermal coupling to regeneration fluids (a fundamental issue that needs to be addressed, most immediately by employing thin MLCs)	Demonstration of HVAC systems, and other applications such as portable coolers for medicine.
		Improve EC ceramic compositions with acceptable COP and low cost / low environmental impact raw materials		
		Research into new materials (material discovery)		
	Ferroelectric polymers	Explore new, ferroelectric polymers with high, field-dependent spontaneous polarizations		
	Organics and Molecular ferroelectrics, e.g. TTF-QBrCl3	Basic research into molecular ferroelectrics (e.g. research to reduce leakage)		
		Explore different schemes for ferroelectricity in organics (e.g. H-transfer, displacement, charge transfer. Flexibility parameter space that can be explored by chemical functionalisation is an advantage. Main issues is that it relies on crystals, which are often small and brittle.		
		Research to improve processing (in thin films?, composites?) and efficiencies		
		Identify strategies to improve the heat transfer limitation (this will have impact beyond the field of electrocalorics, e.g. organics electronics, molecular computing, etc.)		
	Ferroelectric liquid crystals	Ferroelectric liquid crystals are relatively unexplored. Basic research into maximising Ps, polar nematics, hybrid systems, potential of tunability of phase transitions	Potentially developing a family of polar nematic LCs (so far only one or two have been reported, but design rules are accessible)	Demonstration of fluid medium with good enough EC effect
	Hybrid effects/ multicalorics	Research to explore piezoelectrics' ability to modify electrocalorics via strain (and hybrids have been suggested as a way to combine ceramics and polymers)		
System/Device R&D			Demonstration of practical prototype refrigeration systems of domestic size	
			Understanding how to couple the regenerator to the caloric material	
			Identifying what regenerator fluids are appropriate for electrocalorics and the nature of connection/coupling required (e.g. what are the challenges related to fluid dynamics, etc. that need to be overcome?)	
		Research into the electronics to drive the systems/materials (including hybrid systems), e.g. the use of inductive circuitry and sitching techniques to recycle the charge	Understand how to transfer heat out of the EC material, and what materials are compatible electrically and thermodynamically (e.g. solid heat diffusion, sludge flow etc.) and demonstrating these	
		Identify if there are other fabrication technologies for oxides other than the estabished set of processees used for capacitors		
			Some of these issues have probably been addressed in Magnetocalorics - check for overlaps and learn across the effects - perhaps through a joint programme	
Required resources and capabilities		Electronics to drive the systems: Electronic engineers to work on the electronics to drive the systems and materials required (similar to the people that make the MLC structures used in diesel engines)	Demonstration of MLC structures: requires ceramic processing and electrode development; we need a friendly ceramic (capacitor) company, e.g. Murata, AVX, Kyocera?	
		Industry take-up required to make these things happen; need a value proposition and a demonstrator to get a start-up/company interested	Leverage the capacitor technologies being developed for electric cars to further the advancement of MLCs	Develop UK capability for producing high-quality MLCs by importing know-how and personel from collaborators
		Formal/Informal partnerships of leading academics and critical players together across the UK, e.g. into something like the Graphene programme; here all of the caloric strands would be united to address common challenges and share expertise		

Figure 4. Strategic research outlook for Electrocalorics

Elastocalorics

Strengths and weaknesses of elastocalorics

eCs are known to show large thermal changes, and devices could be produced in volume from 10,000 to 100,000 tons per year. Regarding weaknesses, eCs suffer from hysteresis and fatigue, and thermal conductivity is low. Although these materials are usually metals (they can also be polymers[30]), their low thermal conductivity limits the frequency of operation and results in the heat exchange not being fast enough for a viable device. Corrosion could also be an issue and needs to be investigated more[31].

The most critical of these weaknesses is fatigue, both in metals and polymers:[32] *current operation is 10^5 cycles, while ideally it should be 10^9 – 10^{10} cycles to be comparable with currently-deployed heating/cooling technologies.*

The corresponding research for eCs (as defined during the workshop,):

- ***For metals: here fatigue is driven by interfaces, so microstructuring could be the main research focus. Grain boundary engineering or using nucleate precipitates could also be considered.***
- ***For polymers: research could be focused on optimising the amorphous/crystalline ratios and the interaction between organic polymers.***

The strategic research outlook for eC (presented in **Figure 5**) was created in response to these areas of research focus.

Proposed eC research and development initiatives

The following is an outline of the R&D initiatives and the key resources required and included in the eC strategic research outlook shown in **Figure 5**.

- Materials R&D
    - Materials discovery
        - Develop materials with increased thermal conductivity, or improve the thermal conductivity of existing materials
        - Explore composite elastocaloric materials to increase temperature range and strength
    - Research to reduce hysteresis, mechanical breakdown and fatigue
    - Develop precipitates for metals and functional groups for polymers to reduce driving stresses
    - Explore hybrid effects/multicalorics, including
        - Coupling piezoelectric element to an elastic material
        - Piezomagnetic and piezoelectric materials used in combination to generate strain for the piezomagnetic material
        - Magnetostrictive and piezoelectric combinations
        - Exploration of hybrid materials and their use to bypass hysteresis

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[30] eCE has been demonstrated in shape memory polymers (Hong *et al.,* 2019).

[31] Though not expressed explicitly at the workshop, it is important to note some other challenges associated with eC. For example, Cui *et al.* (2015) explained that for useful eC devices, a key challenge is "to develop efficient and inexpensive means to impart the cyclical mechanical stress… typically 400-600 MPa, so the refrigerant can repeatedly and continuously induce the transition", p24, and that the materials can undergo large strains of up to 10%, which must be accommodated within the device and is not always reversible, prompting the need for clever device designs and new eC materials.

[32] This is consistent with the view of Takeuchi & Sandeman (2015) expressed earlier and also with Greco *et al.,* (2019): "The most stringent bottleneck of elastocaloric is represented by the fatigue life of the materials employed; it does not allow the construction of long-lasting devices" p.86.

- System/Device R&D
    - Developing regenerators that operate under compression and do not fail
    - Explore how to achieve lower deformations that would be appropriate for smaller, more compact devices
    - Reduce cost of components
    - Re-use and harvesting of materials and components
    - Implement an efficient way to recover and reuse work to optimise the cooling cycle
    - Explore the use of thermoelectric materials for recovering heat in a hybrid system

There is an assumption that widespread application of eC technology would not be realised if the fatigue issue is not resolved. However, niche applications may still be possible.

Most critical weakness(es)	**Fatigue is the main issue (currently operates in 10^5 cycles) and ideally it should be 10^9 to 10^10 cycles (i.e. the system should be able to run for 10-15 years). Fatigue is an issue for both metals and polymers.**
Corresponding research challenges/foci	**For metals, fatigue is driven by interfaces so microstructuring could be the main research focus. Grain boundary engineering or using nucleate precipitates could also be considered. For polymers the research focus could be on optimising the amorphous to crystalline ratios and the interaction between the organic polymers.**

		Short term (Present - 2025)	Medium term (2025 - 2035)	Long term (2035 - 2050)
Material R&D	Elastocaloric materials	Materials discovery	Demonstrate high energy efficiency	
		Improve (reduce) hysteresis and mechanical breakdown *(some work is done in Germany and in the USA that demonstrated improvements in fatigue)*	Explore composite elastocaloric materials to increase temperature range and strength	
		Improve (reduce) fatigue *(which takes on different forms in polymers and is related to many different factors, e.g. cross link breakage, amorphous phase of polymers/monomers used. Applying strain before doing any cycling actually improves fatigue)*	Develop materials with increased thermal conductivity or improve the thermal conductivity of existing materials. New materials should exhibit large ΔS and ΔT	
			Understand and minimise hysteresis to reduce driving stress and and losses	
			Develop precipitates for metals and functional groups for polymers to reduce driving stress	
	Hybrid effects/ multicalorics	Explore: a) coupling a piezoelectric element to an elastocaloric material - this exploits the large entropy changes occurring in the elastocaloric material allowing them to be accessed via an electrical drive b) piezomagnetic and piezoelectric combinations used in combination to generate strain for the piezomagnetic material c) magnetostrictive and piezoelectric combinations	Explore hybrid materials, and their use to bypass hysteresis	
System/Device R&D			Improve cooling performance i.e. by increasing cycle frequency and reducing heat losses	
			Reduce cost of components (this is anticipated as the technology is scaled-up)	
		Developing regenerators that operate under compression and do not fail *Building regenerators is a challenge, and if driven in compression (which is better for fatigue) the design and fabrication of the elastocaloric elements is not straightforward. For example, typically one has to manufacture pipes with NiTi and this is complex and not very easy. Finding ways of driving these big changes in an energy efficient way is necessary. Current mechanical methods are not very efficient.*	Develop heat switches that are heat leak free, fast and have large ON/OFF ratio and could operate under high stress.	
			Lifetime analysis (on accelerated timescales) that show robust properties in all components for at least 10 years	
			Re-use and harvesting of materials and components	
		Explore how to achieve lower deformations or strain that will be required to make smaller devices. *An important challenge for materials (e.g. classic elastomers liquid crystals) is that the strains are very large (approximately 10%), which is a barrier to device fabrication*	Implement an efficient way to recover and re-use work to optimise the cooling cycle. *This can be done electrically (from a capacitor to an inductor e.g. an electrical flywheel). A large amount of work is done on diesel fuel piezoelectric multilayer actuators for the automotive industry. Could also exploit magnetic transition for magneto-thermal regeneration*	
			Explore the use of thermoelectric materials for recovering heat in a hybrid system	
Required resources and capabilities		Access to more Synchrotron and Neutron facilities - maybe to have priority access		
		Funding for man-power in materials engineering and discovery, systems engineering, characterisation, computational materials modelling and thermal modelling. *Not many people work in this area in the UK in the bulk materials. Many people work on thin films.*		
		Funding for the development of bespoke experimental systems and equipment to measure certain parameters, for example large temperature changes. *This is not trivial and requires a multi-disciplinary development of components, sensors etc.*		
		Funding for networks - perhaps with EPSRC support *(see the following EPSRC-relevant links: https://epsrc.ukri.org/funding/calls/decarbonising-heating-and-cooling/ and https://epsrc.ukri.org/newsevents/news/decarbonising-heating-and-cooling-for-net-zero-survey-of-needs/)*	Industrial partnerships (with companies in air-conditioning, refrigeration, manufacturing, start-ups etc.)	
			Standardisation of Safety and Performance. This should be done through ISO or CEN but the UK should have work items to take to ISO or CEN for consideration and inclusion into standards.	
		Have a *Faraday Partnership* for refrigeration. *There was a partnership for Cooling led by Birmingham University (Birmingham Energy Institute), called CleanCool (see https://www.birmingham.ac.uk/research/energy/research/cold-economy/cooling-energy-challenge.aspx and https://www.birmingham.ac.uk/Documents/college-eps/energy/Publications/2018-clean-cold-report.pdf)*		

Figure 5. Strategic research outlook for Elastocalorics

Barocalorics

Strengths and weaknesses of barocalorics

The large thermal response of barocaloric materials (already comparable to current fluids used for vapour compression in standard refrigeration) is encouraging but the driving pressures required are an order of magnitude too high (in order to overcome large thermal hysteresis). The main issue is how to apply the required pressures in a practical manner (currently in the region of 2,000 bar). Identifying materials with reduced thermal hysteresis will reduce the applied pressures required. The relatively low density of BCs could be an issue for certain applications where compact heating/cooling is required (e.g. commercial refrigeration) and the ability to use work-recovery processes to improve efficiency is also important.
According to the experts, the most critical of these weaknesses are:

i. *high driving pressures required, linked to large thermal hysteresis of the material. This is an order of magnitude higher than conventional refrigeration.*
ii. *increasing the thermal conductivity to reduce cycle time for certain materials (as per electrocalorics) - this is an issue for organic materials in particular.*

The corresponding BC research challenges were defined as follows:

- ***How might extrinsic hysteresis be reduced?***
- ***How does hysteresis link to entropy change?***
- ***Can a multicaloric cycle that will introduce another driver e.g. magnetic, optical, etc. provide any solution?***

The strategic research outlook for BC (presented in **Figure 6**) was created in response to these challenges.

Proposed BC research and development initiatives

The following is an outline of the R&D initiatives and the key resources required and included in the BC strategic research outlook shown in **Figure 6**.

- Materials R&D
    - Materials discovery – both organic, inorganic, and hybrid organic-inorganic materials – that can exhibit high ΔS and ΔT below driving pressure of <1,000 bar
    - Develop materials with increased thermal conductivity, or improve the thermal conductivity of existing materials
    - Explore composite BC materials to increase temperature range and reduce corrosion
    - Understand and minimise hysteresis to reduce driving pressures and losses; explore hybrid materials and their potential use for bypassing hysteresis

- System/Device R&D
    - Explore alternative mechanical application of pressure, e.g. pumps and piezoelectrics
    - Explore/discover methods for work-recovery, to capture and reuse work when pressure is released
    - Increase thermal conductivity to improve heat exchange under high pressure
    - Explore regeneration of BC devices and material preparation issues
    - Investigate pressure fluids that have high thermal conductivity, low compressibility and are not corrosive

Cross-cutting resource and capability needs

Common resource and capability requirements were identified across the four categories of caloric materials. These are:

- Funding for manpower in materials discovery, materials engineering and systems engineering, materials characterisation, computational materials modelling, and thermal modelling
- Funding for state-of-the-art thermal testing facilities, including bespoke experimental systems and equipment, to develop caloric materials and devices
- Academic-industrial partnerships in manufacturing, air-conditioning, heat pumps and refrigeration technologies
- Standardisation of safety and performance
- *Faraday Partnership* or related forum, consortium or network for zero-carbon cooling and heating for leading academics and critical players across the UK, under which the various areas of research in calorics can collectively address common challenges and share expertise
- Access schemes for synchrotron and neutron facilities for commercial scale-up of caloric systems

A fundamental assumption underpinning the strategic research outlooks is that the UK Government and other key players understand the huge potential of highly energy-efficient zero-carbon cooling and heating technologies – both environmentally and economically – offered by caloric technologies, and that research would be given the crucial support it requires to succeed.

Most critical weakness(es)	- **Driving pressure is linked to hysteresis of the material - reducing the hysteresis will significantly reduce the applied pressures.** - **Improving the thermal conductivity to reduce cycle time for certain materials (as per electrocalorics) - this is an issue for organic materials in particular.**	**Corresponding research challenges**	- **How might extrinsic hysteresis be reduced?** - **How does hysteresis link to entropy change?** - **Can a multicaloric cycle provide any solution, e.g. that will introduce another driver, e.g. magnetic, optical, etc.?**

	Short term (Present - 2030)	**Medium term (2025 - 2035)**	**Long term (2030 - 2040)**
Material R&D			Safety certification (for [new] materials)
	Work on materials discovery - organic and inorganic (including investigating the phase transitions that happen under pressure) *There is still lot of fundamental work that could be done in this area, since this is the least mature domain of caloric materials. New materials should exhibit large ΔS and ΔT and can work below 1,000bar*	Explore composite barocaloric materials to increase temperature range and for reducing corrosion Develop materials with increased thermal conductivity or improve the thermal conductivity of existing materials. New materials should exhibit large ΔS and ΔT and can work below 300bar	
	Explore hybrid materials	Use hybrid materials to bypass hysteresis	
	Understand hysteresis	Understand and minimise hysteresis to reduce driving pressure and losses	
System/ Device R&D	Explore alternative mechanical application of pressure, e.g. pumps and piezo *(for example, coupling a piezoelectric element to a barocaloric material - this exploits the large entropy changes occuring in the large entropy changes occuring in the barocaloric material allowing them to be accessed via an electric drive)*		
	Explore/discover methods for work recovery, i.e. methods to recapture and reuse work when pressure is released *When pressure is under 500 bars, then components that are used for standard hydraulics could be used for these applications as well*	Improve cooling and heating performance i.e. by increasing cycling frequency and reducing heat losses	
	Increase thermal conductivity to improve heat exchange under high pressure; find new materials that have high strength to allow operation under high pressures	Reduce cost of components (this is anticipated as the technology is scaled up) Investigate pressure fluids that have good, high thermal conductivity, low compressibility and are not corrosive	
	Explore regeneration on these devices and material preparation issues (i.e. different morphologies). *For regeneration the materials need to be in certain configurations, e.g. chemical stability when they are in contact with different heat exchange fluids. The regeneration issues are also relevant for single-stage devices*	Develop heat switches that are heat leak free, fast and have large ON/OFF ratio and could operate under high pressure specifically for barocalorics LIfetime analysis (on accelerated timescales) that show robust properties in all components for at least 10 years Re-use and harvesting of materials and components	Scale-up of devices
Required resources and capabilities	Access to more Synchrotron and Neutron facilities - maybe to have priority access		
	Funding for man-power in materials discovery, materials discovery and systems engineering, characterisation, computational materials modelling and thermal modelling.		
	Funding for the development of bespoke experimental systems and equipment to measure certain parameters, for example large temperature changes. *This is not trivial and requires a multi-disciplinary development of components, sensors etc.*		
	Funding for networks - perhaps with EPSRC support *(see the following EPSRC-relevant links: https://epsrc.ukri.org/funding/calls/decarbonising-heating-and-cooling/ and https://epsrc.ukri.org/newsevents/news/decarbonising-heating-and-cooling-for-net-zero-survey-of-needs/)*	Industrial partnerships (with companies in air-conditioning, refrigeration, manufacturing, start-ups etc.) Standardisation of Safety and Performance. This should be done through ISO or CEN but the UK should have work items to take to ISO or CEN for consideration and inclusion into standards.	
	Have a *Faraday Partnership* for refrigeration. *There was a partnership for Cooling led by Birmingham University (Birmingham Energy Institute), called CleanCool (see https://www.birmingham.ac.uk/research/energy/research/cold-economy/cooling-energy-challenge.aspx and https://www.birmingham.ac.uk/Documents/college-eps/energy/Publications/2018-clean-cold-report.pdf)*		

Figure 6. Strategic research outlook for Barocalorics

SUMMARY AND RECOMMENDATIONS

This report, commissioned by the Henry Royce Institute, has focused on caloric technologies, their environmental and economic potential, key challenges preventing their deployment, and an overview of the research required to overcome such challenges.

It explored the potential of caloric technologies to provide a solution for zero-carbon heating and cooling. Caloric materials are solid-state refrigerant alternatives to the prevalent heating and cooling technologies (e.g. use of vapour-compression refrigeration/heat pumping and burning of fossil fuels for space heating), which are fast approaching their limits in energy efficiency and are environmentally harmful. Some caloric technologies are already in production for niche applications but these (and others not yet in production) require significant breakthroughs if they are to have widespread commercial uptake and replace prevalent technologies. The potential environmental and economic opportunities presented by this technology are immense considering that almost 20% of the UK's CO_2 emissions are attributable to space heating and cooling, and that the global market for heating and cooling of buildings (and for commercial and domestic refrigeration) is about £300bn[33]. Success here would not only permit decarbonisation of heating and cooling, but would enable the UK to be a global leader in the net zero-carbon heating and cooling markets, and contribute significantly to energy, environmental and job security.

Four research outlooks were developed based on input from leading UK experts in response to key breakthroughs required – one of each of the four categories of caloric technologies: MC, EC, eC and BC. These include R&D that experts consider critical to deliver the breakthrough required for their development and widespread deployment and application. They show that fundamental and applied research is required across the technology levels (as each of these technologies is at a different maturity level) and that the research would be enabled by close collaboration between academics, and crucially, between academia and key industry players. There is a significant role for Government to play by providing adequate funding to facilitate the technology breakthroughs and accelerated development that is necessary if calorics are to play a meaningful role in helping the UK meet its 2050 net-zero targets, and make the UK a global leader in commercialising and benefitting economically.

It is important that further steps are taken by The Henry Royce Institute and the academic and industrial communities. These should include:

- Helping the Government to further understand the immense potential in caloric technologies for the UK economy and environment, and the need for funding to turn this potential into reality
- Developing partnerships and collaborative systems (across academia and industry) in the UK so that the challenges within and across the caloric effects can be more efficiently and effectively addressed
- Facilitating adequate funding of these partnerships and collaborations enabling basic research (e.g. into materials discovery and development, to overcome some of the key challenges described above), demonstration of prototypes and scale-up to improving cost-efficiencies of components/devices, and UK production capability, e.g. for producing high-quality multi-layer capacitor structures, which is critical to electrocalorics.

[33] Taken from Dr Xavier Moya's presentation at the Materials for Energy Transition Roadmap Webinar. Available at https://www.royce.ac.uk/materials-for-the-energy-transition

REFERENCES

BEIS (2018a). Clean Growth – Transforming Heating. *Department for Business, Energy & Industrial Strategy.* Retrieved 1 July 2020 from https://assets.publishing.service.gov.uk/government/uploads/system/uploads/attachment_data/file/766109/decarbonising-heating.pdf

BEIS (2018b). Business Energy Statistical Summary – How energy is used and by whom in the non-domestic sector. *Department for Business, Energy & Industrial Strategy.* Retrieved 1 July 2020 from https://assets.publishing.service.gov.uk/government/uploads/system/uploads/attachment_data/file/739699/180718_Business_Energy_Statistical_Summary_-_final_version.pdf

BEIS (2019). Energy Consumption in the UK (ECUK). *Department for Business, Energy & Industrial Strategy. Retrieved 1 July 2020 from* https://www.gov.uk/government/statistics/energy-consumption-in-the-uk

BEIS (2020). Final UK Greenhouse Gas Emissions National Statistics: 1990 to 2018. *Department for Business, Energy & Industrial Strategy. Retrieved 1 July 2020 from* https://www.gov.uk/government/statistics/final-uk-greenhouse-gas-emissions-national-statistics-1990-to-2018

Brown, G. V. (1976). Magnetic heat pumping near room temperature. *Journal of Applied Physics*, *47*(8), 3673-3680.

Chaudron, J. B., Muller, C., Hittinger, M., Risser, M., & Lionte, S. (2018). Performance measurements on a large-scale magnetocaloric cooling application at room temperature. In *Proceedings of Thermag VIII, 8th IIR/IIF International Conference on Caloric Cooling*. International Institute of Refrigeration.

Crossley, S., Mathur, N. D., & Moya, X. (2015). New developments in caloric materials for cooling applications. *AIP Advances*, *5*(6), 067153.

Cui, J., Johnson, D. D., Pecharsky, V. K., Takeuchi, I., & Zhang, Q. (2015). Advancing Caloric Materials for Efficient Cooling: Key Scientific and Device-Related Materials Challenges for Impact.

Griffith, L. D., Mudryk, Y., Slaughter, J., & Pecharsky, V. K. (2018). Material-based figure of merit for caloric materials. *Journal of Applied Physics*, *123*(3), 034902.

F-Gas Support (2009) – Guidance on Minimising Greenhouse Gas Emissions from Refrigeration, Air-conditioning and Heat Pump Systems (Information Sheet RAC 7 Alternatives). Retrieved July 1 from https://www.fluorocarbons.org/wp-content/uploads/2009/06/rac_7_refrigerant_selection_new_feb_2009.pdf

Goetzler, W., Shandross, R., Young, J., Petritchenko, O., Ringo, D., & McClive, S. (2017). *Energy savings potential and RD&D opportunities for commercial building HVAC systems* (No. DOE/EE-1703). Navigant Consulting, Burlington, MA (United States).

Gottschall, T., Gràcia-Condal, A., Fries, M., Taubel, A., Pfeuffer, L., Mañosa, L., Planes, A., Skokov, K. P. & Gutfleisch, O. (2018). A multicaloric cooling cycle that exploits thermal hysteresis. *Nature Materials*, *17*(10), 929-934.

Greco, A., Aprea, C., Maiorino, A., & Masselli, C. (2019). A review of the state of the art of solid-state caloric cooling processes at room-temperature before 2019. *International Journal of Refrigeration*, *106*, 66-88.

Gu, H., Qian, X., Li, X., Craven, B., Zhu, W., Cheng, A., Yao, S. C. & Zhang, Q. M. (2013). A chip scale electrocaloric effect based cooling device. *Applied Physics Letters*, *102*(12), 122904.

Guzmán-Verri, G. G., & Littlewood, P. B. (2016). Why is the electrocaloric effect so small in ferroelectrics? *APL Materials*, *4*(6), 064106.

Hess T., Maier L.M., Corhan P., Schafer-Welsen O., Wollenstein J., & Bartholome K., International Journal of Refrigeration 103 (2019) 215-222

Hong, S. B., An, Y., & Yu, W. R. (2019). Elastocaloric effects of carbon fabric-reinforced shape memory polymer composites. *Functional Composites and Structures*, *1*(1), 015004.

Jacobs. S., Auringera, J., A.Boedera, A., Chella, J., Komorowskia, L., Leonard, J., Russek, S., & Zimma, C., (2014) The performance of a large-scale rotary magnetic refrigerator. International Journal of Refrigeration 37, 84-91

Johra, H., Filonenko, K., Heiselberg, P., Veje, C., Lei, T., Dall'Olio, S., Engelbrecht, K. & Bahl, C. (2018). Integration of a magnetocaloric heat pump in a low-energy residential building. In *Building Simulation* (Vol. 11, No. 4, pp. 753-763). Tsinghua University Press.

Kar-Narayan, S., & Mathur, N. D. (2010). Direct and indirect electrocaloric measurements using multilayer capacitors. *Journal of Physics D: Applied Physics*, *43*(3), 032002.

Kitanovski, A., Tušek, J., Tomc, U., Plaznik, U., Ozbolt, M., & Poredoš, A. (2016). *Magnetocaloric energy conversion*. Springer International Pu.

Lloveras, P., Aznar, A., Barrio, M., Negrier, P., Popescu, C., Planes, A., Mañosa, L., Stern-Taulats, E., Avramenko, A., Mathur., N. D. & Moya, X. (2019). Colossal barocaloric effects near room temperature in plastic crystals of neopentylglycol. *Nature communications*, *10*(1), 1-7.

Lu, S.G., Rožič, B., Zhang, Q.M., Kutnjak, Z., Li, X., Furman, E., Gorny, L.J., Lin, M., Malič, B., Kosec, M. & Blinc, R. (2010). Organic and inorganic relaxor ferroelectrics with giant electrocaloric effect. *Applied Physics Letters*, *97* (16), 162904.

Luglietti, R., Rosa, P., Pastore, A., Terzi, S., & Taisch, M., (2017) Life Cycle Assessment Tool Implemented in Household Refrigeration Industry: A Magnetic Cooling Prototype Development, *Procedia Manufacturing*, Volume 8, Pages 231-238

Mañosa, L., González-Alonso, D., Planes, A., Bonnot, E., Barrio, M., Tamarit, J-L., Aksoy, S., & Acet, M. Giant solid-state barocaloric effect in the Ni-Mn-In magnetic shape-memory alloy, *Nature Materials* 9, 478–481, (2010).

Moya, X., Kar-Narayan, S., & Mathur, N. D. (2014). Caloric materials near ferroic phase transitions. *Nature materials*, *13*(5), 439-450.

Moya, X., Defay, E., Mathur, N.D. & Hirose, S. (2018). Electrocaloric effects in multilayer capacitors for cooling applications. *MRS Bulletin.* 43(4), 291.

Moya Raposo, J. E., Avramenko, A., Manosa Carrera, L., Tamarit Mur, J. L., & Lloveras Muntané, P. M. (2020). *U.S. Patent Application No. 16/341,618*.

Moya, X. & Mathur, N.D. (2020). Caloric materials for cooling and heating. *Science 370* (6518) 797-803

Nair, B., Usui, T., Crossley, S., Kurdi, S., Guzmán-Verri, G. G., Moya, X., Hirose, S. & Mathur, N. D. (2019). Large electrocaloric effects in oxide multilayer capacitors over a wide temperature range. *Nature*, *575*(7783), 468-472.

Scheibel, F., Gottschall, T., Taubel, A., Fries, M., Skokov, K. P., Terwey, A., Keune, W., Ollefs, K., Wende, H., Farle, M., Acet, M., Gutfleisch, O., & Gruner, M. E., (2018) *Energy Technol*. 6, 1397.

Stern-Taulats, E., D'Ammaro, A., Avramenko, A., Robinson, A., & Moya, X. (2018). First steps towards barocaloric refrigeration. In *International Conference on Caloric Cooling, Thermag VIII, Darmstadt (Germany)*.

Takeuchi, I., & Sandeman, K. (2015). Solid-state cooling with caloric materials. *Physics today*, *68*(12), 48.

Tassou, S. A., Kolokotroni, M., Gowreesunker, B., Stojceska, V., Azapagic, A., Fryer, P., & Bakalis, S. (2014). Energy demand and reduction opportunities in the UK food chain. *Proceedings of the Institution of Civil Engineers-Energy*, *167*(3), 162-170.

Walton, A., Han Y., Rowson N.A., Speight J.D., Mann, V.J.S., Sheridan, J.S.,. Bradshaw A., Harris, I.R., & William, A.J. (2015). The use of hydrogen to separate and recycle neodymium–iron–boron-type magnets from electronic waste, Journal of Cleaner Production, 104, pp.236-241.

Whatmore, R. W., You, Y.-M., Xiong, R.-G. & Eom, C.-B. (2021) “100 years of ferroelectricity—A celebration” APL Mater. 9, 070401, doi:10.1063/5.0059208

Zhang, T., Qian, X. S., Gu, H., Hou, Y., & Zhang, Q. M. (2017). An electrocaloric refrigerator with direct solid to solid regeneration. *Applied Physics Letters*, *110*(24), 243503.

APPENDICES – WORKSHOP DETAILS

The workshop was commissioned by Henry Royce Institute and delivered by IfM Education and Consultancy Services Limited.

A. WORKSHOP PARTICIPANTS

Delegates

- Professor Neil Alford, Imperial College London / Henry Royce Institute
- Dr Anna-Karin Axelsson, London South Bank University
- Mr William Averdieck, Barocal Ltd
- Professor Lesley Cohen, Imperial College London
- Professor David Dye, Imperial College London
- Dr Finn Giuliani, Imperial College London
- Professor Helen Gleeson, OBE, University of Leeds
- Professor Sandrine Heutz, Imperial College London
- Professor Neil Mathur, University of Cambridge
- Professor Mary Ryan, Imperial College London
- Professor Julie Staunton, University of Warwick
- Professor Roger Whatmore, Imperial College London
- Dr Xavier Moya, University of Cambridge / Barocal Ltd. (Scientific Lead for calorics workshop).

Facilitators

- Dr Imoh Ilevbare, Institute for Manufacturing, University of Cambridge
- Ms. Andi Jones, Institute for Manufacturing, University of Cambridge
- Dr Nicky Athanassopoulou, Institute for Manufacturing, University of Cambridge
- Dr Diana Khripko, Institute for Manufacturing, University of Cambridge
- Dr Arsalan Ghani, Institute for Manufacturing, University of Cambridge
- Dr Lata Sahonta, University of Cambridge / Henry Royce Institute
- Dr Amy Nommeots-Nomm, Imperial College London / Henry Royce Institute
- Isobel Hogg, Institute of Physics.

B. WORKSHOP METHODOLOGY

The methodology adopted was based on wide-ranging engagement with research communities to define the roadmap objectives and expectations, to design and customise the strategic framework for the roadmapping; to develop questionnaires for the research communities involved, and to modify workshop process steps to ensure participation of the entire research community. The workshops brought together academic and industrial experts in the four respective technology areas, and involved both offline and online data collection phases. The offline phases were used for data collection from individual participants and publicly-available research sources, followed by data consolidation and, where necessary and appropriate, prioritisation. The online workshops were used for data review, analysis and deeper exploration of essential issues. The quality and reliability of the process was maintained by a Steering Committee involving roadmapping facilitators and technical leads from each of the four research communities.

In total, 26 workshops sessions were held across the four technology areas between March 2020 and June 2020. These revealed several materials sub-topics of particular interest for contribution towards the net-zero targets, as well as highlighting important fundamental research and commercial technology enablers that need to be established. These outputs significantly aided research communities' understanding of the future direction of energy materials research, towards the achievement UK's net-zero emission targets by 2050.

The roadmapping methodology was used based on the **S-Plan** workshop process framework developed by the IfM over a period of several years [[34], [35], [36]]. The framework has been configured to help universities and research organisations align their research activities with industry needs, supporting decision-making and action. The process followed consisted of three parts: design, the workshops, and reporting of the workshop outcomes.

Design

During the design phase, the following activities took place:

- Discussing and designing in detail the workshop methodology and process.
- Designing the templates necessary to support the workshop activities;
- Agreeing the detailed workshop agenda
- Agreeing the desired workshop outputs.

Workshop agenda

The roadmapping workshop process brought together 13 participants from the research community and industry. The agenda for the five workshop sessions are as follows:

Session 1: 20 March 2020, 14.00 – 16.00

Welcome from HRI	*14:00 – 14:05*
Introductions, objectives and workshop process	*14:05 – 14:20*
Discussing the content collected so far	*14:20 – 14:30*
Review pre-work and identify gaps	*14:30 – 15:30*
Feedback review of group review	*15:30 – 15:55*
Next steps and Close	*15:55 – 16:00*

Session 2: 27 March 2020, 11.00 – 12.00

Introductions and workshop process	*11:00 – 11:10*
Summary of discussions from Session 1	*11:10 – 11:15*
Applications systems and requirements	*11:15 – 11:55*
Next steps and Close	*11.55 – 12.00*

Session 3: 7 April 2020, 13.00 – 14.00

Welcome and introductions	*13.00 – 13.05*
Summary of discussions so far	*13.05 – 13.20*
• *Process so far and overview of information collected*	
• *Observations and proposed process changes*	
Discussions in small groups (per caloric effect):	*13.20 – 13.50*
• *Key issue/weakness per caloric effect*	
Feedback of group discussions	*13.50 – 14:00*
Close	*14.00*

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[34] http://www3.eng.cam.ac.uk/research_db/publications/rp108

[35] Phaal, R., Farrukh, C.J.P., Probert, D.R. (2004). "Customizing Roadmapping", *Research Technology Management,* 47 (2), pp. 26–37.

[36] Phaal, R., Farrukh, C.J.P., Probert, D.R. (2007). "Strategic Roadmapping: A workshop-based approach for identifying and exploring innovation issues and opportunities", *Engineering Management Journal,* 19 (1), pp. 16–24.

Session 4: 9 April 2020, 10.00 – 12.00

Welcome and introductions	*10.00 – 10.05*
Overview of last workshop session	*10.05 – 10.10*
Discussions in small groups per caloric effect	*10.10 – 11.40*
• *Electrocaloric*	
• *Barocaloric*	
Feedback of group discussions	*11.40 – 11.55*
Close	*11.55 – 12.00*

Session 5: 9 April 2020, 13.30 – 15.30

Welcome	*13.30 – 13.35*
Discussions in small groups per caloric effect	*13.35 – 15.05*
• *Magnetocaloric*	
• *Elastocaloric*	
Feedback of group discussions	*15.05 – 15.20*
Next steps and Close	*15.20 – 15.30*

Revisions: July 2021 following input from Dr Neil Wilson (Camfridge Ltd).

C. TABLE OF FIGURES