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Solid-state refrigeration: A comparison of the energy performances of caloric materials operating in an active caloric regenerator

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ABSTRACT

The energy performances of an Active Caloric Refrigerator are reported in this paper. An ACR is tested under a vast number of solid-state refrigerants exhibiting one of the four main caloric effects considered for refrigeration (magnetocaloric, electrocaloric, elastocaloric and barocaloric effect). The analysis is performed numerically through a 2D model, experimentally validated, that can reproduce the behavior of an Active Caloric Regenerator. Temperature span, cooling power and coefficient of performance are the indexes through which the comparison is carried out. The tests are performed at a fixed AMR cycle frequency (1.25 Hz), in the temperature range 292–300 K, varying the mass flux in the range 150–250 $kg\,s^{-1}\,m^{-2}$. The most promising caloric materials that have been tested as refrigerants are: Gd, $Gd_5Si_2Ge_2$, $LaFe_{11.384}Mn_{0.356}Si_{1.26}H_{1.52}$, $LaFe_{11.05}Co_{0.94}Si_{1.10}$ (magnetocaloric materials); P(VDF-TrFE-CFE)/BST polymer, 0.93PMN-0.07PT thin film, the $Pb_{1-3x/2}La_xZr_{0.85}Ti_{0.15}O_3$ with single and variable composition, $PbTiO_3$, $Pb_{0.8}Ba_{0.2}ZrO_3$, $Pb_{0.97}La_{0.02}(Zr_{0.75}Sn_{0.18}Ti_{0.07})O_3$(electrocaloric materials); $Cu_{68.13}Zn_{15.74}Al_{16.13}$, NiTi, $PbTiO_3$ (elastocaloric materials); $(NH_4)_2MoO_2F_4$, $MnCoGe_{0.99}In_{0.01}$ (barocaloric materials). Among them, PLZT and in particular $Pb_{0.97}La_{0.02}(Zr_{0.75}Sn_{0.18}Ti_{0.07})O_3$ show the best results, higher than every other caloric material tested, conferring to electrocaloric refrigeration globally the most promising behavior.

1. Introduction

The world in which we live today is characterized by deep environmental disasters and increasing pollution that results in global warming and sudden climate changes. Today we are the tenants of the world that tomorrow will be inhabited by our progenies. The point is that today we are not able to guarantee them an environmentally friendly future if we do not begin to drastically change the way we live, produce and consume. Demand of energy is growing continuously and more than 20% of energy consumption is due to refrigeration and air conditioning. Even if, over the last two decades, many efforts have already been made to reduce energy consumption, we are still far from acceptable threshold values. Among the many reasons of such data there is also, in some sectors, the still being linked to yesterday's technologies due to the absence of adequate substitutes. As a matter of fact, vapor compression has ruled the market extensively for many years. It is still the predominant technique [1] among industrialized and commercialized refrigerators and HVAC systems, even if it has provoked ozone depletion crisis, due to employment of CFC and HCFC refrigerants whom have been forbidden by Montreal Protocol [2] and substituted by HFCs. HFCs, in turn, have given a big boost to global warming and climate change so that they have been progressively phased out by the Kyoto Protocol [3] and substitutes by other classes of refrigerants (natural fluids, hydrofluoroolefins …) [4]. A more drastic step would be the progressive banning of the vapor compression itself if it could be replaced by a strong alternative. With this in mind, the scientific community has devoted huge efforts in developing possible alternative cooling techniques that would be ecological, performing and characterized by low energy consumptions. Among these alternatives, there is caloric refrigeration [5] that belongs to the solid-state class of cooling techniques also known as non-vapor compression technologies, or not-in-kind (NIK) cooling technologies. They have gained remarkable attention [6] since, taking vapor compression as reference, caloric refrigeration holds a potential for: improvements in energy efficiency; reduction of environmental impact since it employs

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Nomenclature

Symbols

B	magnetic field induction, T
C	specific heat, J kg^{-1} K^{-1}
COP	coefficient of performance, -
E	electric field, V m^{-1}
G	mass flux, kg s^{-1} m^{-2}
H	magnetic field, A m^{-1}
k	thermal conductivity, W m^{-1} K^{-1}
L	length of the regenerator in fluid flow direction
M	magnetization, A m^{-1}
P	polarization, C m^{-2}
p	pressure, Pa
Q	power density associated to caloric effect, W m^{-3}
$\dot{Q}$	power, W
RCP(S)	entropy relative cooling power, J kg^{-1}
RCP(T)	temperature relative cooling power, K^2
S	entropy, J K^{-1}m^{-3}
T	temperature, K
t	time, s
u	longitudinal fluid velocity, m s^{-1}
V	volume, m^3
v	orthogonal fluid velocity, m s^{-1}
$\dot{W}$	mechanical power, W
X	conjugate field
x	longitudinal spatial coordinate, m
Y	applied driving field
y	orthogonal spatial coordinate, m

Greek symbols

Δ	finite difference
δ	infinitesimal difference
ε	strain
$\bar{\varepsilon}$	infinitesimal quantity
η	efficiency, -
θ	period of ACR cycle, s
ν	cinematic viscosity, m^2 s^{-1}
ρ	density, kg m^{-3}
σ	stress, Pa
τ	period of each step of ACR cycle, s

Subscripts

0	minimum
1	maximum
ad	adiabatic
C	cold heat exchanger
CF	cold-to-hot flow process
FWHM	full width at half maximum
f	fluid
FD	field decreasing
FI	field increasing
H	hot heat exchanger
HF	hot-to-cold flow process
MAX	at maximum
p	pump
ref	cooling
rej	heat rejected
S	solid
span	span across ACR cold and hot side

solid-state materials with no direct Ozone Depletion Potential (ODP) and zero direct Global Warming Potential (GWP); reliability and manageability since it is characterized by more compact systems and acoustic comfort due to lower noise levels.

Caloric refrigeration embraces other four main cooling techniques, each one based on a different caloric effect; such physical phenomena are exploited in a growing number of numerical and experimental cooling applications [7]. As a matter of fact, these techniques are linked to the group of materials that show a magnetocaloric, electrocaloric, elastocaloric and barocaloric effect, phenomena where the variation in the temperature of caloric material is registered when an applied external field changes in adiabatic conditions.

Magnetic refrigeration, based on magnetocaloric materials exhibiting a caloric effect under a variation of an external magnetic field, has been the pioneer of caloric cooling since it has been well-studied and investigated for room temperature application over the past thirty years. In truth, the interest in magnetic refrigeration began with the discovery of the magnetocaloric effect attributed to Weiss and Piccard [8] in 1917 but the turning point is located in 1982 when Barclay introduced [9] the use of reciprocating thermal regenerators (Active Magnetic Regenerators) coupled to a thermodynamic cycle, giving rise to a regenerative magnetocaloric cycle called Active Magnetic Regenerative (AMR) refrigeration cycle. The AMR cycle proved to be essential to achieve higher temperature span. The AMR cycle uses MagnetoCaloric Material (MCM) itself as both a refrigerant and regenerator such that the heat transfer process and regeneration process are coupled into a single process. The MCM is heated by magnetization and is cooled by demagnetization. In the last three decades a number of prototypes of magnetocaloric refrigerators has been developed. Most of them is founded on AMR cycle [10–15] classified basing: on rotative or alternative design; else on the nature of magnetic field generator (permanent magnets, superconducting magnets, electromagnets). In 2010, Kitanovski proposed [16] the concept of solid-state magnetic refrigerator founded on the Peltier effect that served as the thermal diode in order to manipulate and control the heat transfer direction. Even if the idea is promising, there are some disadvantages to be accounted like thermal resistance, electric resistance, durability and cost of the Peltier element. Recent studies have identified weaknesses [17,18] points of magnetic refrigeration and tried to improve them [19,20]: as a matter of fact, most of the criticism lays in the high costs in magnetic field generating and the expansiveness of the most promising magnetocaloric refrigerants [21].

Electrocaloric Refrigeration (ER), which found is working principle on ElectroCaloric Effect (ECE), grew in a more recent past [22]. ECE is detected in ferroelectric materials (ElectroCaloric Materials, ECMs) showing an adiabatic temperature change while an applied electric field varies its intensity. Dually to magnetic refrigeration, the reference cycle for such technique is Active Electrocaloric Regenerative (AER) refrigeration cycle. The easy and relatively cheap electric field generation, together with the flexibility in producing high electric fields in large volumes, are the strong points of electrocaloric refrigeration. ER allows theoretically to reach values around 50% of Carnot COP in small-scale applications [23]. A number of promising electrocaloric materials has been developed and most of them has a significant electrocaloric effect in a wider temperature range if compared with magnetocaloric materials [24,25]. Moreover, electrocaloric refrigerants belong