PROCEEDINGS OF ECOS 2015 - THE 28TH INTERNATIONAL CONFERENCE ON
EFFICIENCY, COST, OPTIMIZATION, SIMULATION AND ENVIRONMENTAL IMPACT OF ENERGY SYSTEMS
JUNE 30-JULY 3, 2015, PAU, FRANCE

Present and Future Solid State Energy Conversion Technologies

Andrej Kitanovski[a], Urban Tomc[b], Uroš Plaznik[c] and Alojz Poredoš[d]

a) University of Ljubljana, Faculty of Mechanical Engineering, Ljubljana, Slovenia,
andrej.kitanovski@fs.uni-lj.si (CA)
b) University of Ljubljana, Faculty of Mechanical Engineering, Ljubljana, Slovenia,
urban.tomc@fs.uni-lj.si
c) University of Ljubljana, Faculty of Mechanical Engineering, Ljubljana, Slovenia,
uros.plaznik@fs.uni-lj.si
d) University of Ljubljana, Faculty of Mechanical Engineering, Ljubljana, Slovenia,
alojz.poredos@fs.uni-lj.si

Abstract:

In recent years, several emerging technologies in a domain of solid state physics are being investigated as a serious alternative for future refrigeration, heat pumping, air conditioning, or even the power generation. These technologies regard barocalorics, electrocalorics, magnetocalorics, elastocalorics and recently discovered spin-caloritronics (spin-Seebeck effect). Among the alternatives, the most advanced developments have been performed in the domain magnetic refrigeration. Because of the fact, that many of these technologies represent a potential for improvements in energy efficiency, compactness, sound level, as well as the reduction of the environmental impacts, it is obvious, that they will fulfil certain future market niches as the replacement of the vapour compression principle. The aim of this article is to present and discuss the characteristics of the above mentioned solid state energy conversion technologies, which could serve for further exploitation and future engineering. These regard material requirements and their availability, thermodynamics and energy efficiency, applications or market niches, as well as the foresight of their future developments.

Keywords:

Solid state physics, Energy conversion, Refrigeration, Heat pump, Air conditioning

1. Introduction

One of the major cooling technologies is based on the vapour-compression of a gas refrigerant, and despite of its maturity, it is characterized by the rather low exergy efficiency [1]. In most the cases this technology applies environmentally harmful refrigerants. Despite of the fact that other substances are used as the substitute for existing refrigerants, many of these are also the subject of future prohibition. Several alternatives as the potential replacement of existing refrigerants in the vapour compression, lead to lower energy efficiency [2] and problems related to very high pressures, flammability, explosion hazards, etc. A good alternative to vapour compression are sorption technologies, but their use must be restricted to applications of waste heat utilization, cogeneration (polygeneration) [3], or direct use of heat from renewable energy sources[4]. Other alternative technology is the thermoacoustics [5]. The technology is less efficient than vapour-compression and suffers from relatively low power density [6]. The Peltier cooling is the only solid state refrigeration technology, available on the market. Despite of its advantages that regard miniaturization, no moving parts and silent operation, the technology suffers from the lowest exergy efficiency below 15% [7-9]. A parallel technology to this is the thermionic refrigeration [10]. The problem of thermionics is in its high-temperature operating range (above 230 °C [11]). However thermionic devices show higher efficiencies than thermoelectric devices (above 30 %) [12, 13].Because of the above listed drawbacks of the existing technologies, a new alternative energy efficient and environmentally friendly refrigeration technology is required. Authors of this article believe that future refrigerators and heat pumps will comprise no moving parts, and will operate at high energy efficiency and high power density. This statement is based on the exponential growth of research activities in the domain of solid state energy conversion (Fig. 1). Four of these new technologies, namely the magnetocaloric, electrocaloric, barocaloric, and elastocaloric energy conversion regard the group of the so called caloric materials. Two technologies, the magnetocaloric energy conversion and the electrocaloric energy conversion have already been presented at previous ECOS conferences [14-16]. The aim of this article is therefore not to repeat existing information, but a continuation of a series of articles, which we dedicate to new solid state energy conversion technologies.

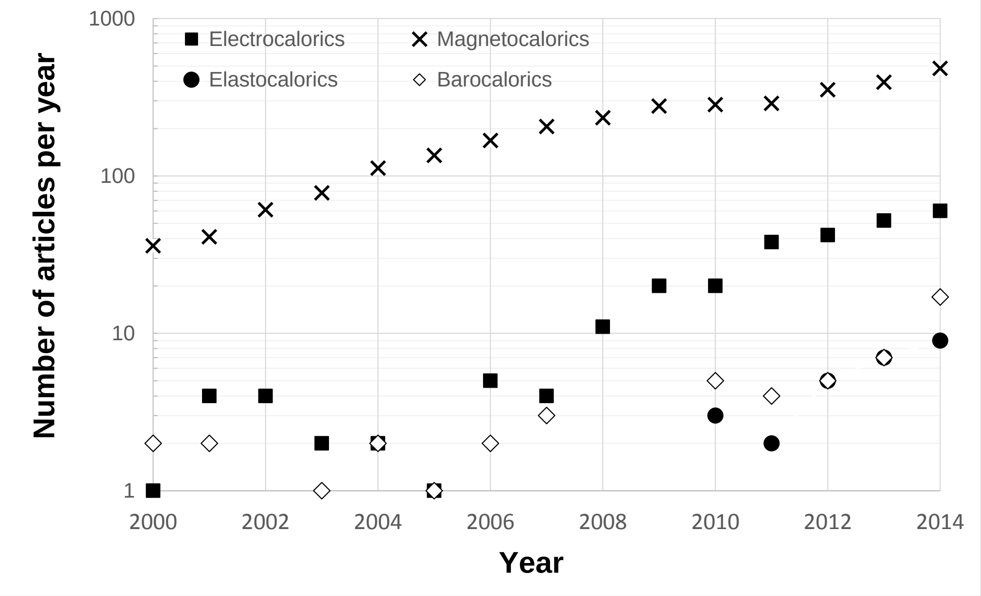

Fig. 1. The number of yearly published articles per domain (by use of the Web of Science and key words "magnetocaloric", "electrocaloric", "elastocaloric" and "barocaloric").

2. Caloric solid state refrigeration or heat pump technologies

The operation of a thermodynamic refrigeration cycle in all the caloric technologies is analogue. When the caloric material is exposed to a change of an external field, i.e. by magnetization (magnetic refrigeration), polarization (electocaloric refrigeration), stretching (elastocaloric refrigeration), and (com)pression (barocaloric refrigeration), the caloric material heats up. This process in analogue to the compression of a gas refrigerant. The generated heat due to the caloric effect is rejected out of the system (analogue to condensation). For this purpose heat transfer process is established. In the third process, which is analogue to the expansion of gas refrigerant, the caloric material is again exposed to the change of an external field (its decrease), i.e. the demagnetization (magnetic refrigeration), depolarization (electocaloric refrigeration), release (elastocaloric refrigeration), and expansion (barocaloric refrigeration) of the caloric material decreases its temperature. The next process is related to the heat transfer in which the caloric material accepts heat from the cooled environment (heat transfer from the heat source to the caloric material (Fig. 2). Caloric materials will exhibit larger temperature changes if the applied or released field change is higher. However large changes in applied fields (magnetic, electric, stress or pressure fields) are related to the energy input, weight or volume of the field source (especially in magnetocaloric energy conversion), and finally the costs. In magnetocaloric, elastocaloric (especially thick and bulk ceramics), and barocaloric refrigeration or heat pumping, the applied fields are mostly related to small field changes, therefore small temperature changes of caloric materials (e.g. 0.5 to 4 K). For a realistic refrigeration or heat pump cycle, this temperature span is of course far then sufficient. One way to increase such a temperature span is the use of cascade devices. However, the overlapping of thermodynamic cycles in this case will not lead to a very efficient solutions. More efficient process is the active caloric regenerative process [17].

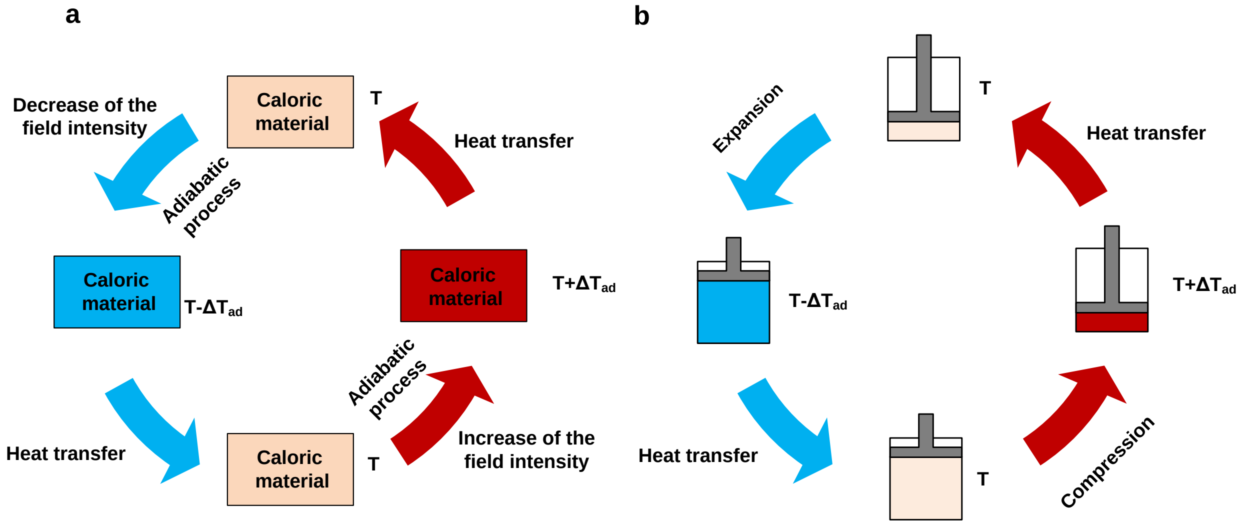

Fig. 2. (a) Schematic presentation of the energy conversion cycle (refrigeration or heat pumping) with a caloric material. The caloric material can be considered magnetocaloric, electrocaloric, elastrocaloric or barocaloric. Correspondingly the material is subjected to the magnetic, electric, stress or pressure field change (b) A classical vapour-compression energy conversion cycle.

More information on active regenerative process can be found in our previous contributions to ECOS [14-16]. The active caloric regenerative process is one best known solutions, however this principle is strongly restricted by the efficiency of the convective heat transfer in the regenerator. Since the fluid flow through the regenerator made of caloric material is oscillatory, this somehow also restricts the efficiency of an active heat regeneration process, especially at high power density. Presently known alternative to active heat regeneration is the application of thermal diode mechanism. More on this principle can be again found in the series of our ECOS articles [14-16]. Note that the most comprehensive information on application of the active regeneration as well as thermal diode mechanisms can be found in our latest book on magnetocaloric energy conversion [18].

2.1. Magnetocaloric energy conversion

Magnetocaloric energy conversion at or near room temperature is a relatively new and still developing technology, which applies materials with the magnetocaloric (MC) effect. The technology represents a potential to be more efficient than comparable conventional vapour-compression refrigeration or heat pumping [19-20]. Since Brown [21] designed the world’s first magnetic refrigerator operating at room temperature in 1976, more than 60 different prototypes were built up to today [18]. However, scientific research hasn’t been able to bring the technology to the point of commercialization so far. One of the key issues is certainly inefficient heat transfer between the MC material and the working fluid, which influences two main working parameters of MC devices: the temperature span and the operating frequency (a number of thermodynamic cycles per unit of time). The later affects the specific cooling power (cooling power per mass of the MC material). The magnetocaloric effect is not sufficiently large for the operating temperature span of the realistic magnetic refrigerator. Application of the Active Magnetic Regeneration (AMR) concept overcomes this problem to some extent in a manner that the MC material may now exploit not only the MC effect, but also the process of the heat regeneration. The most representative MC material is gadolinium (Gd), which reaches its highest MC effect at 20°C. Experimental analyses done on Gd showed the highest temperature spans of 25-30 K [22-26]. These could be improved with better AMR’s geometry. Since MC materials are limited by their temperature operating range, the introduction of layered AMR with several different MC materials along the regenerator can solve this problem. In this manner the ability to achieve higher temperature spans can be strongly improved, what has been already experimentally proven

[27]. The most prospective groups of MC materials are Gd and its alloys [18], La-Fe-Si based materials [28], Mn based materials [29], manganites [30, 31] and Hausler compounds [32, 33]. Selected magnetocaloric materials are presented in Table 1.

Table 1: Some of the selected, promising magnetocaloric materials

Material	T_C (K)	$-\Delta s_M$ ($Jkg^{-1}K^{-1}$)	ΔT_{ad} (K)	ΔB (T)	Ref.
Gd	~293	3.1	3.3	1	[34]
$Gd_{0.9}Tb_{0.1}$	~286	2.3	1.9	1	[35]
$Gd_5Si_2Ge_2$	~278	14	7.3	2	[36]
$LaFe_{11.06}Co_{0.86}Si_{1.08}$	~276	6.1	2.3	1	[34]
$LaFe_{10.96}$ $Co_{0.97}Si_{1.07}$	~289	5.3	2.2	1	[34]
$La(Fe_{0.88}Si_{0.12})_{13}H$	~274	19	6.2	2	[37]
$La(Fe_{0.89}Si_{0.11})_{13}H_{1.3}$	~291	24	6.9	2	[37]
$MnFeP_{0.45}As_{0.55}$	~306	12.5	2.8	1	[38]
$Mn_{1.1}Fe_{0.9}P_{0.47}As_{0.53}$	~292	11	2.8	1	[38]
$Ni_{45.2}Mn_{36.7}In_{13}Co_{5.1}$	~317	18	6.2	2	[39]
$La_{0.67}Ca_{0.33}MnO_3$	~267	5.9	2.0	1.2	[40]
$La_{0.67}Ca_{0.275}Sr_{0.055}MnO_3$	~285	2.8	1	1.2	[40]

In the Table 2, some of the most important characteristics of the present stage of magnetocaloric refrigeration technology are presented. Despite of the fact that a relatively large number of prototypes have been built worldwide, these are still limited in the efficiency to the operating frequencies up to 5 Hz, to temperature spans of 15 to 20 K, and to specific cooling powers up to 200 W/kg [26,42-45]. These limitations are mostly affected by the heat transfer. However the operating characteristics, especially the cooling power and the temperature span, are gradually improving.

Table 2: Some characteristics of magnetocaloric refrigeration and heat pumping technology

Advantages	Drawbacks	Future R&D
- no hysteresis of certain materials - cyclic stability - no Joule heating with permanent magnets - very high potential exergy efficiency - silent operation, no vibration	- moving parts with permanent magnets - Joule heating with electric resistive magnets - rare-earth materials in permanent magnets - expensive rare-earth magnets - manufacturability of regenerators - moderate magnetocaloric effect	- improve and implement new manufacturing and processing methods for regenerators - apply thermal diodes for particular solutions with high power density - use solutions for higher magnetocaloric effect $\Delta T>4–5$ K - apply good working fluids - avoid use of rare earths - search for solutions without moving parts

The economic aspects of the magnetic refrigeration at room temperature have been addressed in several economic analyses [46-48]. On the other hand, Kitanovski and Egolf [19] have shown that present concepts of devices (AMR) will not be able to efficiently operate above operating frequencies of 5 to 10 Hz. Due to all the described issues, an alternative research approach, proposed by Kitanovski and Egolf [49] is emerging in the field of the magnetic refrigeration at room temperature. It involves a whole new concept of the AMR, which would apply so called thermal diodes. Generally one can distinguish between solid state thermal diodes and microfluidic thermal diodes [18]. Several theoretical studies regarding the new concept of the AMR with thermal diodes have been presented in the past few years [50-53]. Their common conclusion is that thermal diodes could indeed drastically increase operating characteristics, especially operating frequencies (even above 100 Hz) and consequently specific cooling powers (even above 10 kW/kg). However the experimental proof-of-the-concept is still required.

2.2. Electrocaloric energy conversion

The electrocaloric energy conversion is an alternative heat pumping technology based on materials with the electrocaloric effect (ECE). This effect is analogous to the magnetocaloric effect, however instead of the magnetic field change an electric field change is required to induce the temperature or entropy change of the material [54-56]. The electrocaloric energy conversion can be advantageous over the magnetocaloric energy conversion. The reason lies mainly in the way how the electric field change can be generated in comparison with the magnetic field change. Instead of using permanent, rare-earth magnets, the electric filed change can be generated using simple voltage generators or electric power convertors plugged into electric grid. Therefore, the mass, the size and the cost of an electrocaloric energy conversion device can be substantially decreased in a comparison with a magnetocaloric energy conversion device [57]. Recent research activities show [55, 58-60] that the magnitude of the electrocaloric effect can be of an order higher than the magnitude of the magnetocaloric effect (achievable with permanent magnets), what is also related to the achievable power density of an electrocaloric device [57,18]. There are two main groups of electrocaloric materials: ceramics and polymers. Usually these are in a form of thin plates, with their thickness ranging from a few tens of nanometers (thin film materials) to a few hundreds of microns (bulk materials). When choosing the best electrocaloric material for an energy conversion device, the same set of criteria as in the case of magnetocaloric energy conversion [18] can be used: suitable temperature of the phase transition (near the phase transition the ECE is usually the largest), the intensity of the ECE, the wide temperature range of the ECE, near-zero hysteresis of the ECE, high thermal conductivity and diffusivity, good manufacturing properties and high electrical resistivity. There are several review articles [55, 61-62] in which electrocaloric materials are reviewed and their properties listed. The materials exhibiting the largest values of the ECE, in a range up to few tens of degrees kelvin, are usually in form of thin films (thickness < 1 μm) or thick films (thickness > few tens of μm) and possess relatively poor mechanical properties. In order to apply these materials in an electrocaloric energy conversion device, they should be further processed into a sort of a multilayer structure made of electrocaloric material with electrodes to enhance their mechanical properties [61]. Based on the available information we have selected some of the most perspective electrocaloric materials. Their characteristics are presented in the Table 3.

Table 3: Some of the selected, promising electrocaloric materials

Material	Form	ΔT_{ad} (K)	ΔE (MVm^{-1})	d (μm)	T* (K)	Ref.
P(VDF-TrFE-FCE)/BNNSs/BST67	Thick film polymer with nanocomposite	50.5	250	6	T_{room}	[63]
PLZT 8/65/35	Thin film ceramic	40	120	0.4	318	[58]
PMN	Bulk ceramic	2.6	8.8	80	340	[64]

A property of some thick and thin films is that they can withstand high electric field changes, leading to high ECE. The reason why the PMN bulk ceramic material was included in the selection, though it exhibits ECE almost 20 times smaller than P(VDF-TrFE-FCE)/ /BNNSs/BST67 and PLZT 8/65/35, is that in contrast to P(VDF-TrFE-FCE)/BST67 and PLZT 8/65/35, the PMN bulk ceramic does not need to be further processed into the so called multilayer structure. Parallel to discovering new materials with the ECE, different concepts of electrocaloric energy conversion devices have been proposed [61, 65-69]. In general, these concepts can be divided into devices based on the use of thermal diode mechanisms [65], and devices based on the active heat regeneration [61, 67, 68], respectively. However, just few of the concepts were experimentally tested [67, 68, 70], and all of them apply active heat regeneration. Their characteristics are presented in Table 4. As can be seen from the Table 4, the ECE materials used in the first experimental devices exhibit much lower adiabatic temperature changes than the adiabatic temperature changes of the materials listed in the Table 3. Therefore, by developing processing technique for the best electrocaloric materials and implementing these materials into cooling devices their performance can be substantially improved. Furthermore, the characteristic of devices can be further enhanced by optimizing their geometrical properties and operating conditions, which influence the heat transfer between the electrocaloric material and the heat sink and heat source of the device.

Table 4: Characteristics of experimental electrocaloric cooling devices

Author	Year	Short description	ΔT_{ad}[a]	ΔT_{exp}[b]	Cooling power	Ref.
Sinyavsky and Brodyansky	1991	Device with internal heat regeneration	1.3 K at 3 MVm^{-1}	5 K at 6 MVm^{-1}	No load	[67]
Gu et al.	2013	Device with solid state regenerator	2.25 K at 80 MVm^{-1}	6.6 K at 100 MVm^{-1}	No load	[68]
Plaznik et al.	2014	Device with active heat regenerator	0.89 K at 5 MVm^{-1}	3.3 K at 5 MVm^{-1}	No load	[70]

[a] Adiabatic temperature change of the electrocaloric material used in the device

[b] Temperature diference between the hot and the cold end of the electrocaloric device

In the Table 5, we show some of the most important features and guidelines for the electrocaloric refrigeration and heat pumping.

*Table 5**:** Some characteristics of the electrocaloric refrigeration and heat pumping technology*

Advantages	Drawbacks	Future R&D
- cyclic stability in some cases - no Joule heating in some materials - can be designed for micro-scale appl. - no moving parts - moderate or large electrocaloric effect - silent operation, no vibration - large electrocaloric effect in polymers and thin film ceramics	- manufacturability of regenerator - need to regenerate electric energy input for better efficiency - similar potential exergy efficiency than magnetocaloric - moderate electrocaloric effect in bulk and thick film ceramics	- improve and implement new manufacturing and processing methods for materials and regenerators - regenerate electricity - apply thermal diodes for particular solutions with high power density - use solutions for higher electrocaloric effect $\Delta T > 4–5$ K - apply good working fluids

2.3. Barocaloric energy conversion

The barocaloric energy conversion is based on the property of some materials whose temperature changes upon varying the pressure [62]. Similar to the electrocaloric or magnetocaloric effect a barocaloric material heats up as the pressure is increased and cools down as the pressure is decreased. Properties of some barocaloric materials are presented in Table 6.

Table 6: Properties of some barocaloric materials

Material	ΔT_{ad} (K)	Applied pressure field Δp (GPa)	T[a] (K)	Ref.
NiMnIn	4.5	0.26	273	[72]
$Ce_3Pd_{20}Ge_6$	0.75	0.3	4.4	[73]
$Pr_{0.66}La_{0.3}4NiO_3$	0.1	0.5	350	[74]

[a] Temperature at which ΔT_{ad} was measured

In comparison with the recent intensive research of the magnetocaloric and electrocaloric materials, the materials with the barocaloric effect attained considerably less attention from the research community [18]. Furthermore, to the best knowledge of the authors, only one conceptual design of a barocaloric energy conversion device has been proposed [75] and even in this case, the authors stated, that the concept was only used to demonstrate the barocaloric refrigeration process. In the future, new, improved materials with the barocaloric effect should be developed together with new prototype devices.

2.4. Elastocaloric energy conversion

The elastocaloric effect is related to the temperature increase of a material because of the applied stress (strain) or temperature decrease after releasing the stress. This effect was first observed in the Indian rubber (shape memory polymer) in the early 19th century (Moya et al [42]). About 50 years later Joule reported on the elastocaloric effect in some metals and dry woods. The first analyses of the elastocaloric effect came much later in 1980s, and were performed for superelastic, shape-memory materials, based on Cu and Ni-Ti alloys [76-79]. The first study which proposed the elastocaloric effect to be applied in cooling applications was published in 1992 by Nikitin et al. [80]. They measured a negative adiabatic temperature change of 5.2 *K* in a polycrystalline $Fe_{49}Rh_{51}$ alloy, under the stress removal. In 2013 the group from the University of Barcelona reported on the elastocaloric effect with the negative adiabatic temperature change of 6 *K* (range between 200 and 350 *K)* for a single-crystalline $Cu_{68}Zn_{16}Al_{16}$, [81]. Their earlier theoretical work, based on the Clausius-Clapeyron relation, estimated the adiabatic temperature change to be 15 *K* [82]. In 2012, Cui et al. [83] reported on analyses of the elastocaloric effect in polycrystalline Ni-Ti wires. A positive adiabatic temperature change of 25.5 *K* was measured during the mechanical loading and a negative adiabatic temperature change of 17 *K* for unloading. Additional work on these kinds of alloys has been performed by Ossmar et al. [84] on $Ni_{50.4}Ti_{49.6}$ thin films. They reported on the 16 *K* of negative adiabatic temperature change under stress removal (unloading). Another experimental and theoretical work on the Ni-Ti wire has been reported by Tušek et al [85]. They measured the largest adiabatic temperature change during loading of 25 K. During unloading process at 322 K, they measure the negative temperature change of 21 K. In 2012, Bechtold et al. [86] published results of their analyses on the electrocaloric effect and the functional stability of the $Ti_{54.9}Ni_{32.5}Cu_{12.6}$ thin film, and performed a comparison of characteristics with the $Ni_{50.4}Ti_{49.6}$ alloy. Their results reveal, that by adding the Cu to the Ni-Ti alloy, the stability of the superelastic behaviour is strongly increased. However it also reduces the electrocaloric effect (negative adiabatic change of 6 *K*). All the above-presented elastocaloric materials exhibit the first-order phase transition, which is related to the hysteresis behaviour and irreversibilities. However, in 2013 Xiao et al. [87] reported on the elastocaloric effect of the single-crystalline $Fe_{68.8}Pd_{31.2}$, which represents the second-order material, with the continuous structural phase transition and near-zero hysteresis. The adiabatic temperature change of about 2.5 *K* was measured, which is rather small effect, however without the hysteresis. In the same year Guyomar et al. [88] analysed the elatocaloric effect of the shape-memory polymer natural rubber and measured an adiabatic temperature change of 10 *K*. In the Table 7 we show a list of some of the most interesting and experimentally validated elastocaloric materials. With regard to conceptual elastocaloric prototype devices, the first such device has been developed in 1994 by DeGregoria [89]. This device applied a shape-memory polymer (natural rubber) in the form of thin layers (foils). These were then constructed into a porous regenerator with thin voids for the air as the heat transfer fluid. The operation of a device was based on the active regenerative process. Four such regenerators were applied into the eccentric rotary system (in order to balance forces). During the operation two regenerators where loaded (stretched) and the other two regenerators were unloaded (unstretched). The authors reported on the 19 K of temperature span. In 2012, a group from the University of Maryland [90] patented various ideas for applications of the elastocaloric effect. In 2014, the same group reported on the numerical investigation of dynamic performances of the elastocaloric air-conditioner [91]. By following different news on the web it seems that the group had also realized the real prototype device. In 2014 and 2015, Schmidt et al (reported by Moya et al [92]) have developed an experimental elastocaloric heat pump device, based on a ribbon of the superelastic shape memory alloy NiTi. Other elastocaloric devices, which have been developed in this particular domain, serve mostly for the evaluation of the elastocaloric effect of different shape memory materials or alloys and do not represent a refrigeration or a heat pump. One of the main limits of elastocaloric matierals or refrigeration technology is related to a rather large mechanical-thermal hysteresis of the elastocaloric materials (first order materials, which also exhibit the largets elastocaloric effect). Another problem is related to the cycling stability of elastocaloric materials.

Table 7: Properties of some elastocaloric materials [18, 77]

Material	Austenitic transition temperature T [K]	Measured adiabatic temperature change ΔT_{ad} [K]	Estimated a) ΔT_{ad} [K]	Estimated* isothermal entropy change Δs_{is} [$Jkg^{-1}K^{-1}$]	Applied field $\Delta\sigma$ [Mpa] or Elongation $\Delta\varepsilon$ [%]	Ref.
$Fe_{49}Rh_{51}$	305	5.2 K (unloading)	8.7 K (unloading)	13 $Jkg^{-1}K^{-1}$ (unloading)	529 MPa	[80]
$Cu_{68}Zn_{16}Al_{16}$	200 – 350	5 K (at 225 K) and 7 K (at 325 K) both for unloading	15 K (at 300 K) for loading	16 $Jkg^{-1}K^{-1}$ (between 225 and 325 K) for loading	275 MPa	[81,82]
Ni-Ti	295	25.5 K (loading), 17 K (unloading)	N.A.	N.A.	650 MPa	[83]
$Ni_{50.4}Ti_{49.6}$	near room temp.	16 K (unloading)	N.A.	N.A.	5 %	[84]
$Ni_{48.9}Ti_{51.1}$	312-342	25 K (loading), 21 K (unloading) at 322 K	N.A.	35.1 $Jkg^{-1}K^{-1}$ for loading 33.9 $Jkg^{-1}K^{-1}$ for unloading	800 Mpa 6%	[85]
$Ti_{54.9}Ni_{32.5}Cu_{12.6}$	346	5 K (loading) 6 K (unloading)	N.A.	N.A.	2 %	[86]
$Fe_{68.8}Pd_{31.2}$	260	2.5 K (loading and unloading)	3.5 K (loading and unloading)	N.A.	100 MPa	[87]
Natural rubber	297	10 K (loading)	N.A.	N.A.	70 %	[88]

a) using Clausius-Clapeyron relation

Table 8: Some characteristics of the elastocaloric refrigeration or heat pump technology

Advantages	Drawbacks	Future R&D
- large elastocaloric effect influences high exergy efficiency of a potential device (especially if hysteresis problem will be solved) - cheap materials	- cyclic instability - moving parts - manufacturability of regenerator - hysteresis of materials influences the decrease in energy efficiency	- remove (reduce) hysteresis - increase cyclic stability - design and develop appropriate regenerator's structure - search for solutions without moving parts - apply thermal diodes for particular solutions with high power density

3. Conclusion

In this article we have briefly presented four different caloric technologies, the magnetocaloric, electrocaloric, elastocaloric and barocaloric refrigeration and heat pumping, respectively. Because of their large potential, we can name them as the future solid state energy conversion technologies. Therefore, for the most of these technologies we predict, that they will play an important role as the replacement of future small vapor compression based refrigerators, small heat pumps, small vehicle air conditioners, replacement of Peltier cooling, and other potential thermal management technologies, as well as some small energy harvesters. Strong research efforts are still required, as well as the strong and interdisciplinary collaboration on the international level, supported with the involvement of strategic industrial partners.

Acknowledgement

We would like to thank Dr. Jaka Tušek from Danish Technical University for valuable remarks and suggestions.

References

[1] Paul J., Quo vadis, heat pump?. In: Proceddings of the 23rd International IIR Congres of Refrigeration, 2011 Aug 21-26, Prague, Czech Republic, 3920-3927.

[2] Kuijpers L.J.M., Refrigeration within a climate regulatory framework. In: Proceddings of the 23rd International IIR Congres of Refrigeration, 2011 Aug 21-26, Prague, Czech Republic, 7-13.

[3] Deng J., Wang R., Han G., A review of thermally activated cooling technologies for combined cooling, heating and power systems. Progress in Energy and Combustion Science 2011;37(2):172–203.

[4] Kim D., Infante Ferreira C., Solar refrigeration options. Int J Refrig 2008;31(1):3-15.

[5] Zink F., Vipperman J.S., Schaefer L.A., Environmental motivation to switch to thermoacoustic refrigeration. App Therm Eng 2010;30:119-126.

[6] Brown D.R., Stout T., Dirks J., Fernandez N., The Prospects of Alternatives to Vapor Compression Technology for Space Cooling and Food Refrigeration Applications. Energ Eng 2012;109:7-20.

[7] Zhao D., Tan G., A review of thermoelectric cooling: Materials, modelling and applications. App Therm Eng 2014;66:15-24.

[8] Goldsmid H.J., Introduction to Thermoelectricity. Springer Series in Materials Science, Springer, 2010.

[9] B. Bhushan (Ed.), Encyclopaedia of Nanotechnology, Springer, 2012.

[10] Hatsopoulos G.N., Kaye J., Measured thermal electron engine. J Appl Phys 1958;29:1124-1125.

[11] Yeom J., Shannon M.A., Micro-coolers. Elsevier, New York, 2008.

[12] Bean J.A., Thermionic refrigeration. Lectures on advanced semiconductor devices. Department of Electrical Engineering, University of Notre Dame, Notre Dame, 2010.

[13] Lough B.C., Lee S.P., Lewis R.A., Zhang C., Numerical calculation of thermionic cooling efficiency in a double barrier semiconductor heterostructure. Physica E 2001;11:287–291.

[14] Kitanovski A., Tušek J., Poredoš A., The magnetocaloric energy conversion. In: ECOS 2012: Proceedings of the 25th International Conference ECOS; 2012 Jun 26-29; Perugia. 97-1-97-13.

[15] Kitanovski A., Plaznik U., Poredoš A., Recent developments in electrocaloric refrigeration. In: ECOS 2014: Proceedings of the 27th International Conference ECOS; 2014 Jun 15-19; Turku, Finland. 1-12.

[16] Kitanovski A., Tušek J., Ožbolt M., Tomc U., Plaznik U., Poredoš A., New solid state refrigeration technologies. In: ECOS 2013: Proceedings of the 26th International Conference ECOS; 2013; Guilin, Jianzhong, China.1-15.

[17] Barclay, J.A., Steyert, W.A., Active magnetic regenerator, US Patent 4.332.135. 1982

[18] Kitanovski A., Tušek J., Tomc U., Plaznik U., Ožbolt M., Poredoš A., Magnetocaloric energy conversion: From theory to applications. Series: Green energy and technology. Springer Publications, 2015.

[19] Kitanovski A., Egolf P.W., Application of magnetic refrigeration and its assessment, J Magn Magn Mater 2009; 321:777-781.

[20] Tassou S.A., Lewis J.S., Ge Y.T., Hadawey A., Chaer I., A review of emerging technologies for food refrigeration applications, App Therm Eng 2010;30:263-276.

[21] Brown G.V., Magnetic heat pumping near room temperature, J Appl Phys 1976;47:3673-3680.

[22] Tušek J., Kitanovski A., Poredoš A., A comprehensive experimental analysis of gadolinium active magnetic refrigeration. App Therm Eng 2013;53:57-66.

[23] Sari O., Balli M., From conventional to magnetic refrigerator technology. Int J Refrig 2014;37:8-15.

[24] Tura A., Rowe A., Progress in the characterization and optimization of a permanent magnet magnetic refrigerator. In: Third IIF-IIR Thermag Conference; 2009 May 11-15; Des Moines, Iowa, USA. 387-392.

[25] Arnold D.S., Tura A., Ruebsaat-Trott A., Rowe A., Design improvements of a permanent magnet active magnetic refrigerator. Int J Refrig 2014;37:99-105.

[26] Engelbrecht K., Eriksen D., Bahl C.R.H., Bjørk R., Geyti J., Lozano J.A., Nielsen K.K., Saxild F., Smith A., Pryds N., Experimental results for a novel rotary active magnetic regenerator, Int J Refrig 2012;35:1498-1505.

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

[28] Shen B.G., Sun J.R., Hu F.X., Zhang H.W., Cheng Z.H., Recent progress in exploring magnetocaloric materials. Adv Mater 2009;21:4545-4564.

[29] Brück E., Tegus O., Cam Thanh D.T., Trung N.T., Buschow K.H.J., A review on Mn based materials for magnetic refrigeration: Structure and properties. Int J Refrig 2008;31:763-770.

[30] Phan M.H., Yu S.C., Review of the magnetocaloric effect in manganite materials. J Magn Magn Mater 2007;308:325-40.

[31] Markovich V., Wisniewski A., Szymczak H., Magnetic Properties of Perovskite Manganites and Their Modifications, in: Buschow, K.H.J. (Ed.), Handbook of Magnetic Materials, Vol. 22, Elsevier B.V.; 2014.

[32] Moya X., Kar-Narayan S., Mathur N.D., Caloric materials near caloric phase transitions. Nat Mater 2014;13:439-450.

[33] Gottschall T., Skokov K.P., Frincu B., Gutfleisch O., 2015. Large reversible magnetocaloric effect in Ni-Mn-In-Co. Appl Phys Lett 2015;106:021901.

[34] Bjørk R., Bahl C.R.H., Katter M., Magnetocaloric properties of $LaFe_{13-x-y}Co_xSi_y$ and commercial grade Gd. J Magn Magn Mater 2010;322:3882-3888.

[35] Kaštil J., Javorský P., Kamarád J., Magnetocaloric effect of Gd-Tb alloys: influence of the sample shape anisotropy. Appl Phys A 2011;104:205-209.

[36] Pecharsky V.K., Gschneidner Jr. K.A., Giant magnetocaloric effect in $Gd_5(Si_2\ Ge_2)$. Phys Rev Lett 1997;78:4494.

[37] Fujita A., Fujieda S., Hasegawa Y., Fukamichi K., Intinerant-electron transition and large magnetocaloric effects in $La(Fe_xSi_{1-x})_{13}$ compounds and their hydrides. Phys Rev B 2003;67:104416.

[38] Brück E., Ilyn M., Tishin A.M., Tegus O., Magnetocaloric effects in $MnFeP_{1-x}As_x$ – based compounds. J Magn Magn Mater 2005;290-291:8-13.

[39] Liu J., Gottschall T., Skokov K. P., Moore J. D.,Gutfleisch O., Giant magneto caloric effect driven by structural transitions. Nat Mater 2012;11:620-26.

[40] Dinesen A.R., Linderoth S., Mørup S.,Direct and indirect measurements of the magnetocaloric effect in $La_{0.67}Ca_{0.33-x}Sr_xMnO_{3\pm\delta}$ ($x \in [0;0.33]$). J Phys Condens Matter 2005;17:6257-6269.

[41] Yu B.F., Liu M., Egolf P.W., Kitanovski A., A review of magnetic refrigerator and heat pump prototypes built before the year 2010. Int. J. Refrig. 2010;30:1029-60.

[42] Zimm C., Boeder A., Chell J., Sternberg A., Fujita A., Fujieda S., Fukamichi K., Design and performance of a permanent-magnet rotary refrigerator. Int. J. Refrig. 2006;29:1302-06.

[43] Zimm C., Auringer J., Boeder A., Chell J., Russek S., Sternberg A.,Design and initial performance of a magnetic refrigerator with a rotating permanent magnet. In: Poredoš A., Šarlah A., editors: Proceedings of THERMAG 2; 2007 April 11-13; Portorož, Slovenia. International Institute of Refrigeration: 341-47.

[44] Tura A., Rowe A., Permanent magnet magnetic refrigerator design and experimental characterization. Int. J. Refrig. 2011;34:628-39.

[45] Tušek J., Zupan S., Šarlah A., Prebil I., Poredoš A, Development of a rotary magnetic refrigerator. Int. J. Refrig 2010;33:294-300.

[46] A. Rowe,Configuration and performance analysis of magnetic refrigerators. Int.J.Refrig. 2011;34:168-77.

[47] [Bjørk R., Smith A., Bahl C.R.H., Pryds N., Determining the minimum mass and cost of a magnetic refrigerator. Int. J. Refrig. 2011;34:1805-16.

[48] Kitanovski A., Egolf P.W., Poredos A., Rotary magnetic chillers with permanent magnets. Int. J. Refrig. 2012;35:1055-66.

[49] Kitanovski A., Egolf P.W., Innovative ideas for future research on magnetocaloric technologies. Int. J. Refrig. 2010;33:449-464.

[50] Silva D.J., Bordalo B.D., Pereira A.M., Ventura J., Araujo J.P., Solid state magnetic refrigerator. Appl. Energ. 2012;93:570-74.

[51] Olsen U.L., Bahl C.R.H., Engelbrecht K., Nielsen K.K., Tasaki Y., Takahashi, H. Yasuda Y., Modeling of In-vehicle Magnetic Refrigeration. In: Vasile-Muller C., Egolf P.W., editors. Proceedings of THERMAG 5; 2012 Sep 17-20; Grenoble, France. International Institute of Refrigeration, 557-64.

[52] Egolf P.W., Gravier L., Francfort T., Pawlowski A.G., Courret G., Croci M.,. High-frequency magnetocaloric modules with heat gate operating with the Peltier effect. In: Vasile-Muller C., Egolf P.W., editors. Proceedings of THERMAG 5: 2012 Sep 17-20; Grenoble, France. International Institute of Refrigeration, 61-2.

[53] Tomc U., Tusek J., Kitanovski A., Poredos A., Termoelectric-magnetocaloric energy conversion. In: Vasile-Muller C., Egolf P.W., editors. Proceedings of THERMAG 5; 2012 Sep 17-20; Grenoble, France. International Institute of Refrigeration, 469-76

[54] Correia T., Q. Zhang, editors. Electrocaloric Materials. Springer; 2014.

[55] Valant M., Electrocaloric materials for future solid-state refrigeration technologies. Prog. Mater Sci. 2012;57:980-1009.

[56] Lu S., Rožic B., Kutnjak Z., Zhang Q., Electrocaloric effect (ECE) in ferroelectric polymer films. In: Coondoo I., editor. Ferroelectrics. Rijeka: InTech, 2010. p. 99-118.

[57] Ožbolt M., Kitanovski A., Tušek J., Poredoš A., Electrocaloric vs. magnetocaloric energy conversion. Int. J. Refrigeration 2014;37:16-27.

[58] Lu S., Rožič B., Zhang Q., Kutnjak Z., Li X., Furman E., Gorny L.J., Lin M., Malič B., Kosec M., Organic and inorganic relaxor ferroelectrics with giant electrocaloric effect. Appl. Phys. Lett. 2010;97: 162904.

[59] Zhao Y., Hao X., Zhang Q., A giant electrocaloric effect of a $Pb_{0.97}La_{0.02}(Zr_{0.75}Sn_{0.18}Ti_{0.07})O_3$ antiferroelectric thick film at room temperature. J. Mater. Chem. C 2015;DOI: 10.1039/C4TC02381A.

[60] Bobnar V., Li X., Casar G., Erste A., Glinsek S., Qian X., Zhang Q., Tailoring electrically induced properties by stretching relaxor polymer films. J. Appl. Phys. 2012;111:83515.

[61] Ožbolt M., Kitanovski A., Tušek J., Poredoš A., Electrocaloric refrigeration: Thermodynamics, state of the art and future perspectives. Int. J. Refrigeration 2014;40:74-188.

[62] Scott, J.F., Electrocaloric Materials. Annual Review of Materials Research 2011;41:229-40.

[63] Zhang G., Li Q. Gu H., Jiang S., Han K., Gadinski M.R., Haque M.A., Zhang Q., Wang Q., Ferroelectric Polymer Nanocomposites for Room-Temperature Electrocaloric Refrigeration. Adv Mater 2015;DOI: 10.1002/adma.201404591.

[64] Rožič B., Malič B., Uršič H., Holc J., Kosec M., Kutnjak Z., Direct Measurements of the Electrocaloric Effect in Bulk PbMg1/3Nb2/3O3 (PMN) Ceramics. Ferroelectrics 2011;421:103-7.

[65] Epstein R.I., Malloy K.J., Electrocaloric devices based on thin-film heat switches. J Appl Phys 2009;106:064509.

[66] Karmanenko S.F., Pakhomov O.V.,Prudan A.M.,Starkov A.S., Eskov A., Layered ceramic structure based on the electrocaloric elements working as a solid state cooling line. J Eur Ceram Soc 2007;27:3109-112.

[67] Sinyavsky Y., Brodyansky V., Experimental testing of electrocaloric cooling with transparent ferroelectric ceramic as a working body. Ferroelectrics 1992;131:321-25.

[68] Gu H., Qian X., Li X., Craven B., Zhu W., Cheng A., Yao S.C., Zhang Q.M., A chip scale electrocaloric effect based cooling device. Appl Phys Lett 2013;102:122904.

[69] Gu H., Qian X.-S., Ye H.-J., Zhang Q.M., An electrocaloric refrigerator without external regenerator. Appl Phys Lett 2014;105:162905.

[70] Plaznik U., Tušek J.,Kitanovski A.,Poredoš A.,Numerical and experimental analyses of different magnetic thermodynamic cycles with an active magnetic regenerator. Appl Therm Eng 2013;59(1-2):52-59.

[71] de Oliveira N.A., von Ranke P.J., Troper A., Magnetocaloric and barocaloric effects: Theoretical description and trends. Int J Refrigeration 2014;37:237-48.

[72] Manosa L., Gonzalez-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. Nat Mater 2010;9:478-81.

[73] Strässle T., Furrer A., Dönni A, Komatsubara T., Barocaloric effect: The use of pressure for magnetic cooling in Ce3Pd20Ge6. J Appl Phys 2002;91:8543-45.

[74] Strässle T., Furrer A., Lacorre P., Müller K.A., A novel principle for cooling by adiabatic pressure application in rare-earth compounds. J Alloys Compd 2000;303–304:228-231.

[75] De Oliveira N.A., Barocaloric effect and the pressure induced solid state refrigerator. J Appl Phys 2011;109:053515.

[76] Rodriguez C., Brown LC., The Thermal Effect Due to Stress-Induced Martensite Formation in β-CuAINi Single Crystals. Metallurgical Transactions A 1980;11A:147-50.

[77] Brown LC., The Thermal Effect in Pseudoelastic Single Crystals of β–CuZnSn. Metallurgical Transactions A 1981;12A:1491-94.

[78] Mukherjee K., Sircar S., Dahotre N.B., Thermal Effects Associated with Stress-induced Martensitic Transformation in a Ti-Ni Alloy. Mater Sci Eng 1985;74:75–4.

[79] McCormick P.G., Liu Y., Miyazaki S., Intrinsic thermal-mechanical behaviour associated with the stress induced martensitic transformation in NiTi. Mater Sci Eng A 1993;167:51–6.

[80] Nikitin S.A., Myalikgulyev G., Annaorazov M.P., Tyurin A.L., Myndyev R.W., Akopyan S.A., Giant elastocaloric effect in FeRh alloy. Phys Lett 1992;A 171:234-36.

[81] Manosa L., Jarque-Farnos S., Vives E., Planes A, Large temperature span and giant refrigerant capacity in elastocaloric Cu-Zn-Al shape memory alloys. Appl Phys Lett 2013;103:211904.

[82] Bonnot E., Romero R., Manosa L., Vives E., Planes A., Elastocaloric effect associated with the martensitic transition in shape-memory alloys. Phys Rev Lett 2008;100:125901.

[83] Cui J., Wu Y., Muehlbauer J., Hwang Y., Radermacher R., Fackler S., Wutting M., Takeuchi I., Demonstration of high efficiency elastocaloric cooling with large ΔT using NiTi wires. Appl Phys Lett 2012;101:073904.

[84] Ossmer H., Chluba C., Krevet B., Quandt E., Rohde M., Kohl M., Elastocaloric cooling using shape memory alloy films. Journal of Physics 2013;476:012138.

[85] Tušek, J., Engelbrecht, K., Mikkelsen, L.P., Pryds, N., Elastocaloric effect of Ni-Ti wire for application in a cooling device. J Appl. Phys 2015; Accepted.

[86] Bechtold C., Chluba C., Lima de Miranda R., Quandt E., High cyclic stability of the elastocaloric effect in sputtered TiNiCu shape memory films. Appl Phys Lett 2012;101:091903.

[87] Xiao F., Fukuda T., Kakeshita T., Significant elastocaloric effect in a Fe-31.2Pd (at. %) single crystal. Appl Phys Lett 2013;102:161914.

[88] Guyomar D., Li Y., Sebald G., Cottinet J.P., Ducharne B., Capsal J.F., Elastocaloric modeling of natural rubber. Appl Therm Eng 2013;57:33-38.

[89] DeGregoria AJ., Elastomer bed. International Patent 1994; WO 94/10517.

[90] Cui J., Takeuchi I., Wuttig M., Wu Y., Radermacher R., Hwang Y., Muehlbauer J., Thermoelastic cooling. US 2012/0273158 A1.

[91] Qian, S., Ling, J., Hwang, Y., Radermacher, R., Dynamic Performance of a Compression Thermoelastic Cooling Air-Conditioner under Cyclic Operation Mode. Proceedings of the 15th International Refrigeration and Air Conditioning Conference; 2014 Jul 14-17; Purdue, USA. Paper 1411.

[92] Moya, X., Defay, E., Heine, V., Mathur, N.D., Too cool to work, NATURE PHYSICS 11, 2015; 202-205