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Dynamic tuning by hydrostatic pressure of magnetocaloric properties to Ericsson like cycles

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ABSTRACT

A method to increase the relative cooling power to be used in Ericsson like refrigeration cycles is presented. The technique is based in the modification of the magnetic properties by the application of hydrostatic pressure on magnetic samples. The main advantage is to reach larger values of the magnetic entropy change in a wider temperature region (the so-called "table like" behavior). The study was carried out in a manganite belonging to the family of $La_{0.625-y}Nd_yCa_{0.375}MnO_3$, and some conclusions were compared with the expected behavior in other materials extracted from literature.

1. Introduction

Magnetic refrigeration has been proposed as one of the most promising technologies to replace conventional refrigerators, which operate by gas compression-expansion cycles [1].

Refrigerators based in the use of the magnetocaloric effect (MCE), present a large number of benefits compared with gas based ones, providing a higher energy efficiency and avoiding the use of greenhouse gases.

The MCE has been widely used for cooling applications at low temperature taking advantage of the adiabatic demagnetization presented by many paramagnetic salts. However, the use of MCE in room temperature refrigeration is, at this moment, in experimental stage in research laboratories.

The observation of large MCE at room temperature in Gd based compounds, has motivated the scientific community to increase its efforts and a lot of research has been dedicated to the study to this particular topic seeking for a material with large MCE at room temperature and low cost of production. A large number of different families of compounds were proposed to replace Gd, such as As based compounds [2], heusler alloys [3], LaFe(Si,La) [4] and mixed-valence manganese oxides (manganites) [5].

Manganites were widely studied a decade ago due to the colossal magnetoresistance effect, a thousandfold reduction of the electrical resistivity that can potentially be used in magnetic reading heads and magnetic data storage devices. Besides, the magnetic properties of manganites can be easily tuned by different mechanisms, such as strain in thin films [6], grain size [7] and cation substitution [8]. This characteristic combined with the low cost of production positioned to manganites as one of the plausible materials to be used in MCE applications.

The MCE can be quantified by the entropy change produced by the application of the magnetic field (ΔS), being its temperature dependence typically characterized by a peak around the transition temperature.

In order to manipulate the magnetocaloric properties of a system it is possible to apply a hydrostatic pressure on it. Depending of the system this can result in an enlargement of the entropy change [9–11] or in the modification of the transition temperature, resulting in a displacement of the temperature where the maximum entropy change is reached [12,13]. Even more, the use of pressure to induce or assist a magnetic transition has been proposed due to its proficiency to favor magnetic ordering [14].

The relative cooling power (RCP) defined as the product of the maximum entropy change and the temperature width of the peak is another magnitude to consider when a material is being analyzed [15]. A large RCP implies a large temperature range where the material will be suitable to produce an adequate cooling effect considering an Ericson like cycle.

To increase the RCP some authors have proposed the use of cascade magnetic cycles [16]. To reach this they use magnetic systems with multiple magnetic transitions, composites [17,18] or layered structures [19] formed by materials with different transitions temperatures. The primary objective of this kind of approach is to obtain an almost constant value of ΔS in the working temperature range obtaining a "table-like" temperature dependence [20]. In that sense Paticopoulos and co-workers [21] studied different mixtures of $Fe_{88-2y}\,Co_y\,Ni_y\,Zr_7\,B_4\,Cu_1$ alloys with $y = 8.25$ and $y = 11$, obtaining the optimal proportion to reach an almost constant entropy change value in a larger temperature region. But, as the width of the entropy change is enlarged, the height is decreased

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when the entropy is normalized with the total mass of the composite. Because of that, the use of composites must be carefully evaluated for each refrigeration device as a particular case.

Gildas Diguet and co-workers analyzed the use of a composite magnetic material in a regeneration Ericsson refrigerator [22]. They used Gd, $Gd_{0.74}Tb_{0.26}$ and $(Gd_{3.5}Tb_{1.5})Si_4$ as the working materials and they conclude that use of the composite represents an improvement when it is compared with the performance of the separated components. The component were selected to obtain a satisfactory magnetocaloric behavior between $T_{cold} = 280\,K$ and $T_{hot} = 300\,K$, meaning that ΔS presents an almost constant value in this temperature range.

In this work we will analyze the possibility to increase the RCP using the hydrostatic pressure as a “dynamic tuner” to reach a “table-like” entropy change dependence with temperature. We will discuss the application of the proposed method in composite samples and compare our results with those extracted from the literature.

2. Materials and methods

Ceramic samples of $La_{0.425}Nd_{0.20}Ca_{0.375}MnO_3$ were obtained by liquid mix as it is described in reference [23]. Magnetization measurements as function of temperature and magnetic field were performed in a Quantum Design Versalab VSM magnetometer. High pressure measurements were obtained using a high pressure cell manufactured by HMD model CC-SPr-8.5-D-MC4-1.

3. Results and discussion

In Fig. 1 we present magnetization as function of temperature for the $La_{0.425}Nd_{0.20}Ca_{0.375}MnO_3$ manganite for different applied magnetic fields (top) and hydrostatic pressure values (bottom). The sample presents a single magnetic transition from a paramagnetic insulator (PI) state at high temperature to a ferromagnetic metallic (FM) at low temperature. The transition temperature increases both by the application of the magnetic field and the hydrostatic pressure consistently with the behavior observed in similar systems13 [24,25].

In order to calculate the entropy change of the system we used the Maxwell relation

$$\Delta S(T,H) = \int_0^H \left(\frac{\partial M}{\partial T}\right)_{H'} dH' \qquad (1)$$

The integral in Eq. (1) can be obtained from isothermal magnetization loops measured at small temperature intervals. In order to avoid an overestimation of the entropy change the sample was carried out to ambient temperature after each magnetization loop [26]. The temperature dependence of ΔS, obtained from Eq. (1), is presented in Fig. 2. In all cases the data presents a peak that can be characterized by three parameters: the maximum (ΔS_{MAX}), the center (T_{MAX}) and the width (quantified by the full width half maximum, δT_{FWHM}).In Fig. 3 (top) we present the dependence of ΔS_{MAX} and the δT_{FWHM} with magnetic field. The value of the ΔS_{MAX} increases with magnetic field, showing a clear tendency towards saturation at 7 J/KgK approximately. In contrast, no significant changes were observed with the application of hydrostatic pressure. In a similar way, the δT_{FWHM} increases almost linearly with the magnetic field but does not show a clear dependence with the hydrostatic pressure.

It has to be noticed that it is not expected to observe a clear dependence of the RCP with the hydrostatic pressure, as neither ΔS_{MAX} nor δT_{FWHM} do.

For the case of T_{MAX} we can observe that both H and P introduce a displacement of the center of the peak towards higher temperatures. This behavior is consistent with the temperature dependence of the magnetization presented in Fig. 1, were both H and P tend to favor ferromagnetic ordering, a fact that can be noticed in the increase of the PI to FM transition temperature.

If we assume a linear dependence of T_{MAX} with H and P, it is possible to fit the center of the peak as $T_{MAX}(H,P) = 198K + 4\frac{K}{T}H + 17\frac{K}{GPa}P$.

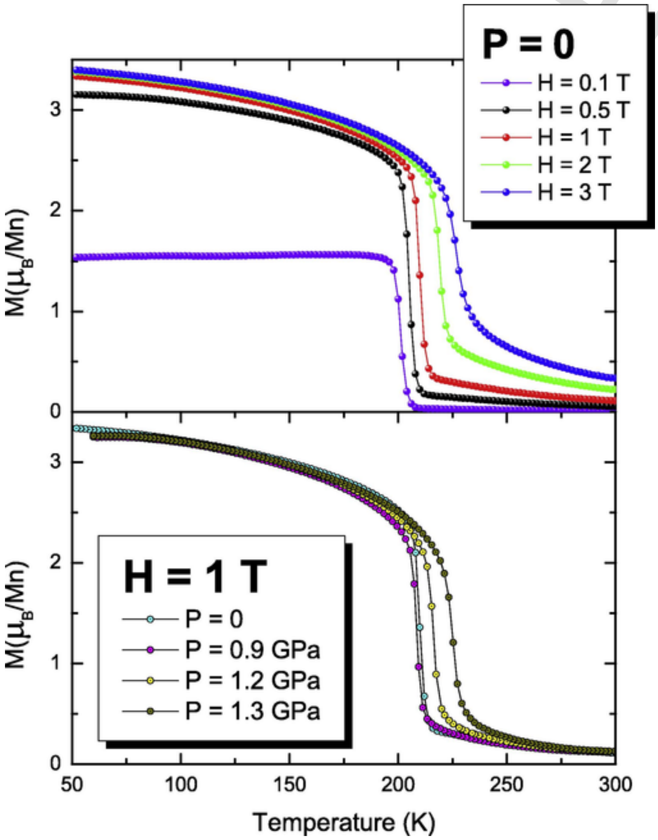

Fig. 1. magnetic moment as function of temperature at ambient pressure and different magnetic fields (top) and at a fixed field of 1 T and varying the hydrostatic pressure (bottom).

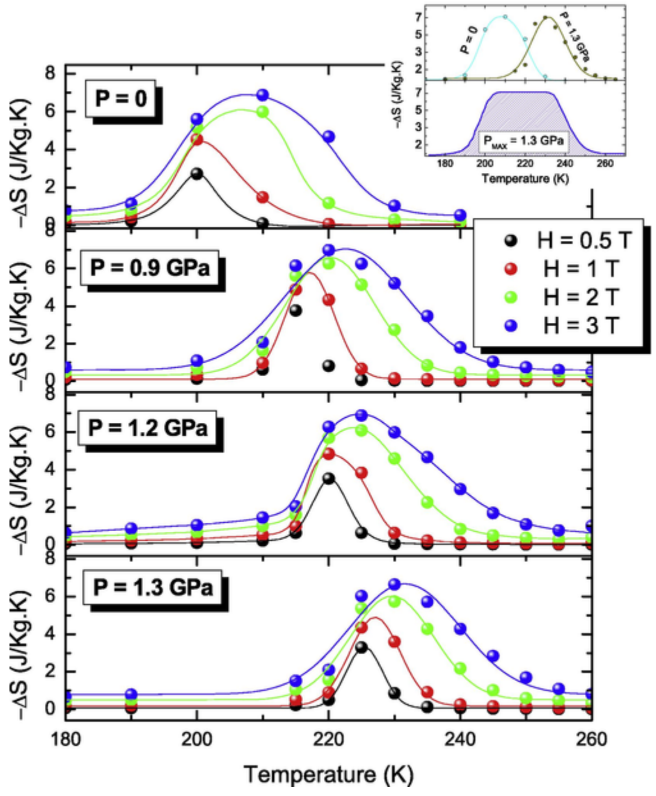

Fig. 2. Entropy change as function of temperature for different magnetic fields and hydrostatic pressure values. In the inset we show how the effective table like behavior can be obtained merging entropy curves with different applied pressure (the applied magnetic field was 3 T).

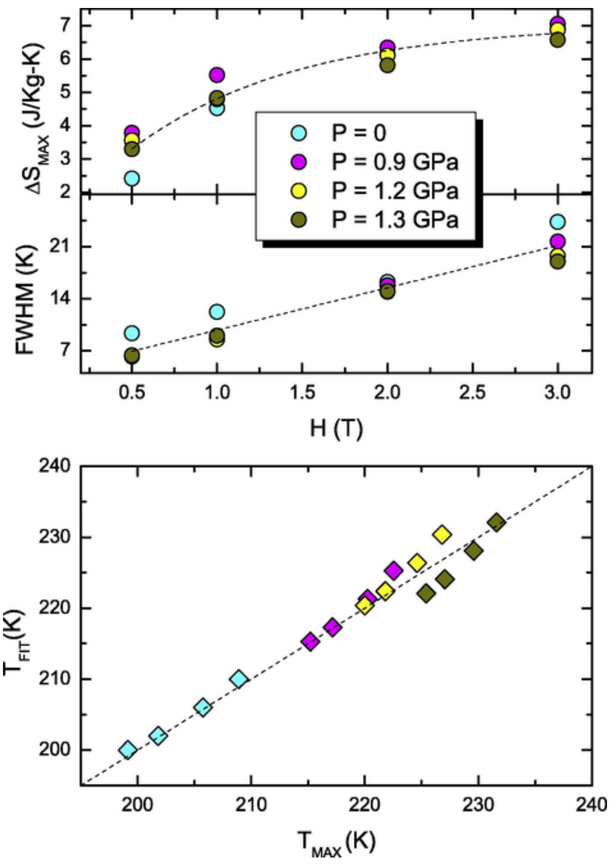

Fig. 3. (Top) Maximum and full width half maximum of the entropy change as function of the applied magnetic field. Colors indicate the value of the hydrostatic pressure. (Bottom) Comparison between the temperature of the center of the peak with the obtained from the proposed magnetic field and pressure dependence. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

This fitting shows that an approximate "equivalence" between the magnetic field and hydrostatic pressure exists in this system. For example, the application of 1 GPa of hydrostatic pressure produces the same effect in T_{MAX} than the application of a 4 Tesla magnetic field.

The above presented results can be used to understand how the magnetic and magnetocaloric properties of this system can be tuned by the application of hydrostatic pressure. The center of the peak can be modified with no significant changes in ΔS_{MAX} and δT_{FWHM}, which are mainly dominated by the magnetic field.

In an oversimplified point of view we can think that the application of hydrostatic pressure modifies the system giving place to a new sample with the same RCP but different T_{MAX}. This resembles the main motivation of the use of composites to obtain a "table-like" entropy change curve. The center of the peak can be tuned in some temperature range by the application of P, depending on the requirements of the magnetocaloric device. Additionally, since the entire sample changes its properties, the efficiency remains unchanged due to the absence of "no-active" regions of sample. To quantify the effect of the application of the pressure in the magnetocaloric capacity we can introduce the *baromagnetocaloric cooling power* (*BMCP*) defined as

$$BMCP = \Delta S_{MAX} \cdot (\delta T_{FWHM} + \Delta T_C^p) \tag{2}$$

where ΔS_{MAX} is the maximum entropy change, δT_{FWHM} is the full width half maximum of the peak and ΔT_C^p is the change in the Curie temperature produced by the application of the hydrostatic pressure.

This quantity can be expressed in terms of the RCP and the rate of change of Tc as

$$BMCP = RCP \cdot \left(1 + \frac{dT_C}{dP} \frac{P_{MAX}}{\delta T_{FWHM}}\right) \tag{3}$$

P_{MAX} is the largest pressure that can be applied and is related with the design of the magnetocaloric device.

In Table 1 we present the values of BMCP relative to the RCP for the $La_{0.425}Nd_{0.20}Ca_{0.375}MnO_3$ sample and for different systems of the literature, considering $P_{MAX} = 1$ GPa.

The value of BMCP can be considered the RCP of a new "virtual" material in which its cooling capacities are extended by the application of the external pressure. It is interesting to note how BMCP becomes larger in those systems where the application of pressure produces an important change in the transition temperature (i.e. $LaFe_{11.6}Si_{1.4}$). In that sense, the compound $La_{0.425}$ $Nd_{0.2}Ca_{0.375}$ MnO_3 is far for being the most reliable choice for this kind of applications, but is a good example to understand our approach.

The main advantage of this approach compared with the use of composites of materials is the absence of efficiency decrease, since the entire sample will be "active" during the application of the magnetic field in the Ericsson like cycle. The obvious disadvantage is the additional complexity in a refrigeration device due to the necessity to control the external pressure. The design of the refrigeration device will include some kind of feedback in order to improve the efficiency of the entire process.

4. Conclusions

Summarizing, we have analyzed the influence of hydrostatic pressure in magnetic samples of $La_{0.425}Nd_{0.2}Ca_{0.375}$ MnO_3 focusing our attention in those parameters that characterize the magnetocaloric effect (i.e. entropy change and relative cooling power). The application of pressure provokes an increase in the ferromagnetic transition temperature in a ratio of 17 K/GPa, keeping the maximum entropy change almost invariant at 7 J/kg·K (for a magnetic field of 3 T). Based on this behavior, we propose the use of pressure to tune the transition temperature as an alternative path (as compared with the use of composites or similar methods) to obtain a "table-like" temperature dependence in the entropy change.

Table 1

Compound	dTc/dP [K/GPa]	DSmax [J/kg·K]	R. C. P [J/kg]	BMCP/RCP	Ref.
$La_{0.425}Nd_{0.2}Ca_{0.375}$ MnO_3	17	7	150	1.5	Present work
$Pr_{0.6}Ca_{0.4}Mn_{0.96}Co_{0.04}O_3$	34.1	7 (P = 0)4.5 (P = .91 GPa)	150	2.7	18
$Pr_{0.6}Ca_{0.4}Mn_{0.96}Cr_{0.04}O_3$	31.1	5 (P = 0)3.5 (P = 0.95)	170	1.91	18
$La_{0.8}Sr_{0.2}MnO_3$	15	6.5 (P = 0)6 (P = .67 GPa)	230	1.45	19
$La_{0.69}Ca_{0.31}$ MnO_3	21.4	7	140	2	20
$LaFe_{11.6}Si_{1.4}$	130	10 (P = 0)40 (P = .83)	50 (P = 0)200 (P = .83)	27	9
$Tb_5Si_2Ge_2$	5.3	13.4	268	1.265	10

To quantify this improvement we have introduced the "baromagnetocaloric cooling power", which takes into account the magnetocaloric response of the system and the "tuneability" of the magnetic transition temperature. We used BMCP to quantify the effect in other systems reported in literature, obtaining a significant increase in all cases.

Even when the application of this particular approach implies an improvement in the cooling capacity, its practical implementation is still challenging, as the application of hydrostatic pressure in a practical device is far from being simple.

References

[1] Andrej Kitanovski, Jaka Tušek, Urban Tomc, Uroš Plaznik, Marko Ožbolt, Alojz Poredoš, Magnetocaloric Energy Conv. (2014).

[2] H. Wada, Y. Tanabe, Giant magnetocaloric effect of MnAs1 − xSbx, Appl. Phys. Lett. 79 (2001) 3302, https://doi.org/10.1063/1.1419048.

[3] A. Planes, L. Manosa, X. Moya, T. Krenke, M. Acet, E.F. Wassermann, Magnetostructural transition and magnetocaloric effect in highly textured Ni-Mn-Sn alloy, J. Magn. Magn. Mater. 310 (2007) 2767. doi: 10.1016/j.jmmm.2006.10.1041; C. Salazar Mejia, A.M. Gomes, N.A. de Oliveira, A less expensive NiMnGa based Heusler alloy for magnetic refrigeration, J. Appl. Phys. 111 (2012) 07A923. doi: 10.1063/1.3675064.

[4] B.G. Shen, J.R. Sun, F.X. Hu, H.W. Zhang, Recent progress in exploring magnetocaloric materials, Adv. Mater. 21 (2009) 4545–4564, https://doi.org/10.1002/adma.200901072.

[5] Manh-Huong Phan, Seong-Cho Yu, Review of the magnetocaloric effect in manganite materials, J. Magn. Magn. Mater. 308 (2007) 325–340. doi: 10.1016/j.jmmm.2006.07.025; A. Rebello, V.B. Naik, R. Mahendiran, Large reversible magnetocaloric effect in La0.7-xPrxCa0.3MnO3, J. Appl. Phys. 110 (2011) 013906. doi: 10.1063/1.3603014.

[6] I. Alessandri, L. Malavasi, E. Bontempi, M.C. Mozzati, C.B. Azzoni, G. Flor, L.E. Depero, Synthesis and characterisation of La1 − xNaxMnO3 + δ thin films manganites, Mater. Sci. Eng. B 109 (1–3) (2004) 203–206, https://doi.org/10.1016/j.mseb.2003.10.046.

[7] P. Levy, F. Parisi, G. Polla, D. Vega, G. Leyva, H. Lanza, R.S. Freitas, L. Ghivelder, Controlled phase separation in La0.5Ca0.5MnO3, Phys. Rev. B 62 (2000) 6437. doi: 10.1103/PhysRevB.62.6437; M. Quintero, S. Passanante, I. Irurzun, D. Goijman, G. Polla, Grain size modification in the magnetocaloric and non-magnetocaloric transitions in La0.5Ca0.5MnO3 probed by direct and indirect methods, Appl. Phys. Lett. 105 (2014) 152411. doi: 10.1063/1.4898129.

[8] M. Uehara, S. Mori, C.H. Chen, S.W. Cheong, Percolative phase separation underlies colossal magnetoresistance in mixed-valent manganites, Nature 399 (6736) (1999) 560–563, https://doi.org/10.1038/21142.

[9] Young Sun, Z. Arnold, J. Kamarad, Guang-Jun Wang, Bao-Gen Shen, Zhao-Hua Cheng, Pressure enhancement of the giant magnetocaloric effect in LaFe11.6Si1.4, Appl. Phys. Lett. 89 (2006) 172513, https://doi.org/10.1063/1.2372584.

[10] L. Morellon, Z. Arnold, C. Magen, C. Ritter, O. Prokhnenko, Y. Skorokhod, P.A. Algarabel, M.R. Ibarra, J. Kamarad, Pressure enhancement of the giant magnetocaloric effect in Tb5Si2Ge2, Phys. Rev. Lett. 93 (2004) 137201, https://doi.org/10.1103/PhysRevLett.93.137201.

[11] Z. Arnold, C. Magen, L. Morellon, P.A. Algarabel, J. Kamarad, M.R. Ibarra, V.K. Pecharsky, K.A. Gschneider Jr., Magnetocaloric effect of Er5Si4 under hydrostatic pressure, Phys. Rev. B 79 (2009) 144430, https://doi.org/10.1103/PhysRevB.79.144430.

[12] R. Thiyagarajan, S. Esakki Muthu, R. Mahendiran, S. Arumugam, Effect of hydrostatic pressure on magnetic and magnetocaloric properties of Mn-site doped perovskite manganites Pr0.6Ca0.4Mn0.96B0.04O3 (B = Co and Cr), J. Appl. Phys. 115 (2014) 043905, https://doi.org/10.1063/1.4862810.

[13] Daniel L. Rocco, R. Almeida Silva, A. Magnus, G. Carvalho, Adelino A. Coelho, José P. Andreeta, Sergio Gama, Magnetocaloric effect of La0.8Sr0.2MnO3La0.8Sr0.2MnO3 compound under pressure, J. Appl. Phys. 97 (2005) 10M317, https://doi.org/10.1063/1.1856891.

[14] M. Quintero, G. Garbarino, A.G. Leyva, Hydrostatic pressure to trigger and assist magnetic transitions: baromagnetic refrigeration, Appl. Phys. Lett. 104 (2014) 112403, https://doi.org/10.1063/1.4868866.

[15] K.A. Gschneidner Jr., V.K. Pecharsky, Magnetocaloric materials, Annu. Rev. Mater. Sci. 30 (2000) 387, https://doi.org/10.1146/annurev.matsci.30.1.387.

[16] J. Romero Gómez, R. Ferreiro Garcia, A. De Miguel Catoira, M. Romero Gómez, Magnetocaloric effect: a review of the thermodynamic cycles in magnetic refrigeration, Renew. Sustain. Energy Rev. 17 (2013) 74–82, https://doi.org/10.1016/j.rser.2012.09.027.

[17] A.G. Gamzatov, A.M. Aliev, A.R. Kaul, Magnetocaloric effect in La1-xKxMnO3 (x = 0.11, 0.13, 0.15) composite structures in magnetic fields up to 80 kOe, J. Alloys Compd. 710 (2017) 292, https://doi.org/10.1016/j.jallcom.2017.03.300.

[18] M. Pekała, K. Pekała, V. Drozd, K. Staszkiewicz, J.-F. Fagnard, P. Vanderbemden, Magnetocaloric and transport study of poly- and nanocrystalline composite manganites La0.7Ca0.3MnO3/La0.8Sr0.2MnO3, J. Appl. Phys. 112 (2012) 023906, https://doi.org/10.1063/1.4739262.

[19] A.M. Aliev, A.G. Gamzatov, I. Kamilov, A.R. Kaul, N.A. Babushkina, Magnetocaloric properties of La0.7Ca0.3Mn16O3 and La0.7Ca0.3Mn18O3 manganites and their "sandwich", Appl. Phys. Lett 101 (2012) 172401, https://doi.org/10.1063/1.4761953.

[20] A. Smaïli, R. Chahine, Composite materials for Ericsson-like magnetic refrigeration cycle, J. Appl. Phys. 81 (1997) 824, https://doi.org/10.1063/1.364166.

[21] S.C. Paticopoulos, R. Caballero-Flores, V. Franco, J.S. Blázquez, A. Conde, K.E. Knipling, M.A. Willard, Enhancement of the magnetocaloric effect in composites: experimental validation, Solid State Commun. 152 (2012) 1590–1594, https://doi.org/10.1016/j.ssc.2012.05.015.

[22] Gildas Diguet, Gouxing Lin, Jincan Chen, Performance characteristics of a regeneration Ericsson refrigeration cycle using a magnetic composite as the working substance, Int. J. Refrig. 36 (2013) 958–964, https://doi.org/10.1016/j.ijrefrig.2012.11.022.

[23] J. Sacanell, P. Levy, A.G. Leyva, F. Parisi, L. Ghivelder, Phase diagram of La5/8 − yNdyCa3/8MnO3 manganites, J. Phys.: Condens. Matter 19 (2007) 186226, https://doi.org/10.1088/0953-8984/19/18/186226.

[24] R. Thiyagarajan, S. Esakki Muthu, R. Mahendiran, S. Arumugam, Effect of hydrostatic pressure on magnetic and magnetocaloric properties of Mn-site doped perovskite manganites Pr0.6Ca0.4Mn0.96B0.04O3 (B = Co and Cr), J. Appl. Phys. 115 (2014) 043905, https://doi.org/10.1063/1.4862810.

[25] Young Sun, J. Kamarad, Z. Arnold, Zhi-qi Kou, Zhao-hua Cheng, Tuning of magnetocaloric effect in a La0.69Ca0.31MnO3La0.69Ca0.31MnO3 single crystal by pressure, Appl. Phys. Lett. 88 (2006) 102505, https://doi.org/10.1063/1.2183824.

[26] L. Caron, Z.Q. Ou, T.T. Nguyen, D.T. CamThanh, O. Tegus, E. Bruck, On the determination of the magnetic entropy change in materials with first-order transitions, J. Magn. Magn. Mater. 321 (2009) 3559–3566, https://doi.org/10.1016/j.jmmm.2009.06.086.