Direct and inverse magnetocaloric effect in half-doped $La_{0.5}Ca_{0.5}MnO_3$ and $Pr_{0.5}Sr_{0.5}MnO_3$

Effet magnétocalorique direct et inverse dans les composés semi-dopés $La_{0,5}Ca_{0,5}MnO_3$ et $Pr_{0,5}Sr_{0,5}MnO_3$

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ABSTRACT. In this communication, we report the magnetic and magnetocaloric study of $Pr_{0.5}Sr_{0.5}MnO_3$ and $La_{0.5}Ca_{0.5}MnO_3$ compounds prepared by solid-state reaction at high temperature. The temperature dependence of magnetization indicates that each sample displays two distinct magnetic transitions: when decreasing temperature, each sample undergoes a paramagnetic-ferromagnetic transition followed by a ferromagnetic-antiferromagnetic transition. The magnetocaloric study indicates that both samples are the seat of direct (near the paramagnetic-ferromagnetic transition) and inverse (near the ferromagnetic-antiferromagnetic transition) magnetocaloric effect. The inverse magnetocaloric effect is more important for $Pr_{0.5}Sr_{0.5}MnO_3$ compound due to the absence of magnetic phase separation.

RÉSUMÉ. Dans cette communication, nous avons effectué l'étude magnétique et magnétocalorique des composés $Pr_{0,5}Sr_{0,5}MnO_3$ et $La_{0,5}Ca_{0,5}MnO_3$ préparés par la méthode solide-solide à haute température. L'évolution de l'aimantation en fonction de la température indique que chaque composé montre deux transitions magnétiques distinctes : lorsque la température diminue, chaque composé passe de l'état paramagnétique à l'état ferromagnétique, cette transition est suivie par une autre transition vers un état antiferromagnétique. L'étude magnétocalorique indique que les deux échantillons sont le siège d'un effet magnétocalorique direct (au voisinage de la transition paramagnétique-ferromagnétique) et inverse (au voisinage de la transition ferromagnétique-antiferromagnétique). L'effet magnétocalorique inverse est plus important pour le composé $Pr_{0.5}Sr_{0.5}MnO_3$ suite à l'absence du phénomène de séparation des phases magnétiques.

KEYWORDS. Manganite, charge ordering, phase separation, magnetocaloric effect.
MOTS-CLÉS. Manganite, ordre de charges, séparation de phases, effet magnétocalorique.

1. Introduction

Half-doped manganites with general formula $Re_{0.5}Ae_{0.5}MnO_3$ (with Re a lanthanide and Ae an alkaline earth element) are still fascinating the scientific community due to the remarkable phenomena they display. These compounds can exhibit more than one magnetic transition as a function of temperature. Besides, several intriguing phenomena are linked to those compounds like charge ordering, orbital ordering, magnetic phase separation, kinetic arrest, training effect [BOU 17, DAM 98, DHI 20, DHI 23, KRI 13, KRI 14, KRI 15, KRI 19, SCH 95]…

$Pr_{0.5}Sr_{0.5}MnO_3$ [BOU 17, DAM 98, KRI 14, KRI 19] and $La_{0.5}Ca_{0.5}MnO_3$ [DHI 20, DHI 23, KRI 13, KRI 15, SCH 95] are the most studied half-doped manganites in the recent years. At room temperature, $Pr_{0.5}Sr_{0.5}MnO_3$ possesses a tetragonal symmetry [KRI 19] and $La_{0.5}Ca_{0.5}MnO_3$ crystallizes according to orthorhombic structure [DHI 20]. These two compounds share the fact that both of them exhibit two distinct magnetic transitions as a function of temperature: with increasing temperature, both samples display a first transition from antiferromagnetic to ferromagnetic state, and then from ferromagnetic to paramagnetic state.

The magnetocaloric effect (MCE) is a magnetic field-induced modification in the specimen's temperature. Magnetic materials are the seat of the MCE. Such phenomenon takes place around the paramagnetic-ferromagnetic transition temperature T_C. When studying the MCE in manganites, scientists generally focus on the temperature range in the vicinity of T_C. The MCE around transition temperatures other than T_C is not generally well described. In this work, we have tried to throw some light on the MCE near the antiferromagnetic-ferromagnetic transition for $Pr_{0.5}Sr_{0.5}MnO_3$ and $La_{0.5}Ca_{0.5}MnO_3$ compounds.

2. Experimental techniques

$Pr_{0.5}Sr_{0.5}MnO_3$ and $La_{0.5}Ca_{0.5}MnO_3$ were prepared by conventional solid-state reaction at high temperature. Stoichiometric amounts of extra pure (99.9 % purity, Sigma Aldrich) oxides and carbonates were intimately mixed in an agate mortar and then fired at 600°C. The obtained powder was then pressed into pellets under an axial pressure of 3 tons. The pellets were then fired at 800°C. Several cycles of grinding, pelletizing and sintering were performed until the obtaining of single-phased compounds. In the final cycle, both samples were sintered for 48 hours: $Pr_{0.5}Sr_{0.5}MnO_3$ at 1400°C and $La_{0.5}Ca_{0.5}MnO_3$ at 1200°C. The magnetic measurements were carried out by using a vibrating sample magnetometer in the temperature range 5−330 K and in the magnetic field range 0−8 T. The MCE was computed from isothermal magnetization measurements, based on thermodynamic equations.

3. Results and discussions

The evolution of magnetization as a function of temperature under an applied magnetic field of 0.05 T for both $Pr_{0.5}Sr_{0.5}MnO_3$ and $La_{0.5}Ca_{0.5}MnO_3$ is shown in figure 1. One can observe that each sample demonstrates two distinct magnetic transitions as a function of temperature. For $Pr_{0.5}Sr_{0.5}MnO_3$ compound, the sample undergoes a paramagnetic-ferromagnetic transition with decreasing temperature at T_C = 265 K. This transition is followed by another transition from the ferromagnetic to the antiferromagnetic state at Néel temperature T_N = 160 K. The low temperature magnetic configuration can be described as A-type antiferromagnetism (ferromagnetic planes antiferromagnetically arranged) with the presence of orbital ordering and the absence of charge ordering [DAM 98].

In the case of $La_{0.5}Ca_{0.5}MnO_3$, the sample undergoes a paramagnetic-ferromagnetic transition with decreasing temperature at T_C = 220 K and then one can observe another transition to a charge-ordered antiferromagnetic state at charge ordering temperature T_{CO} = 150 K. The charge-ordered antiferromagnetic state can be described as a CE-type antiferromagnetic configuration where ferromagnetic zigzag chains are antiferromagnetically coupled, leading to an ordering of Mn^{3+} and Mn^{4+} ions according to the three dimensions of the real space [SCH 95]. It is noteworthy that the low temperature magnetic configuration for both samples is different. Besides, one major difference between the two specimens can be observed at low temperature. For $Pr_{0.5}Sr_{0.5}MnO_3$ compound, the magnetization is null at low temperature, indicating a perfect antiferromagnetic structure. However, one can observe that $La_{0.5}Ca_{0.5}MnO_3$ compound possesses an important magnetization value at low temperature, indicating the persistence of some ferromagnetic domains. In fact, the low temperature ground state is characterized by the presence of some ferromagnetic domains trapped inside an antiferromagnetic matrix, testifying the magnetic phase separation phenomenon [SCH 95, KRI 13]. This fact indicates that $La_{0.5}Ca_{0.5}MnO_3$ compound presents a heterogeneous magnetic configuration at low temperature.

For magnetic materials, it is possible to evaluate the MCE from magnetization isotherms based on the Maxwell relation:

$$\Delta S(T,H) = \sum_i \frac{M_{i+1}(T_{i+1},H_i) - M_i(T_i,H_i)}{T_{i+1} - T_i} \Delta H_i \quad [1]$$

where M_i and M_{i+1} are the experimental values of magnetization measured at temperatures T_i and T_{i+1}, respectively, under magnetic applied field H_i. We have used the magnetic field dependence of magnetization (not shown here) to compute the MCE and the results for $Pr_{0.5}Sr_{0.5}MnO_3$ and $La_{0.5}Ca_{0.5}MnO_3$ samples are displayed in figure 2 and figure 3, respectively.

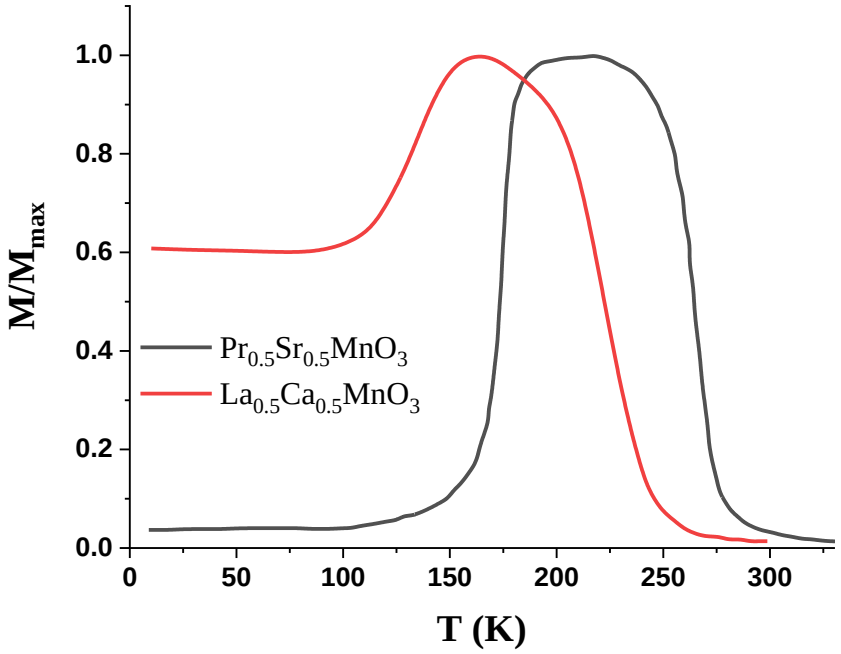

Figure 1. *Temperature dependence of normalized magnetization under 0.05 T applied magnetic field for $Pr_{0.5}Sr_{0.5}MnO_3$ and $La_{0.5}Ca_{0.5}MnO_3$ compounds*

It is clear that both samples exhibits two maximums of magnetic entropy change. The first maximum is located near T_C, and it is a negative one because the ferromagnetic-paramagnetic transition is an order-disorder transition. However, one can observe a positive maximum near T_N for $Pr_{0.5}Sr_{0.5}MnO_3$ and near T_{CO} for $La_{0.5}Ca_{0.5}MnO_3$. The positive values recorded are linked to an order-order transition because each sample exhibits an antiferromagnetic-ferromagnetic transition. The MCE recorded near an antiferromagnetic-ferromagnetic transition is called the inverse MCE, which means that sample gets cooler when an external magnetic field is applied.

By checking the antiferromagnetic-ferromagnetic transition in both figure 2 and figure 3, one can notice two differences between the two positive parts. First, $Pr_{0.5}Sr_{0.5}MnO_3$ sample exhibits higher values of magnetic entropy change compared to $La_{0.5}Ca_{0.5}MnO_3$ sample. Second, the curve shape for $La_{0.5}Ca_{0.5}MnO_3$ sample is the same for all the magnetic field values unlike $Pr_{0.5}Sr_{0.5}MnO_3$ sample where the width of the magnetic entropy change curve drastically increases when the applied field exceeds 2 T. All these observations can be associated to the low temperature magnetic configuration of each sample. Unlike $Pr_{0.5}Sr_{0.5}MnO_3$ where all the sample undergoes the antiferromagnetic-ferromagnetic transition at T_N, the ferromagnetic domains do not contribute to the magnetic entropy change at T_{CO} for $La_{0.5}Ca_{0.5}MnO_3$ sample, leading to lower ΔS values. Besides, the width increases above 2 T field for $Pr_{0.5}Sr_{0.5}MnO_3$ compound because A-type antiferromagnetism is weaker than CE-type characterized by charge-ordering phenomenon.

In order to quantify the MCE, we can consider the relative cooling power (RCP) given by:

$$RCP = \left|\Delta S_{Max}\right| \delta T_{FWHM} \quad [2]$$

where ΔS_{max} is the maximum value of magnetic entropy change and δ_{FWHM} is the full width at half-maximum of the peak.

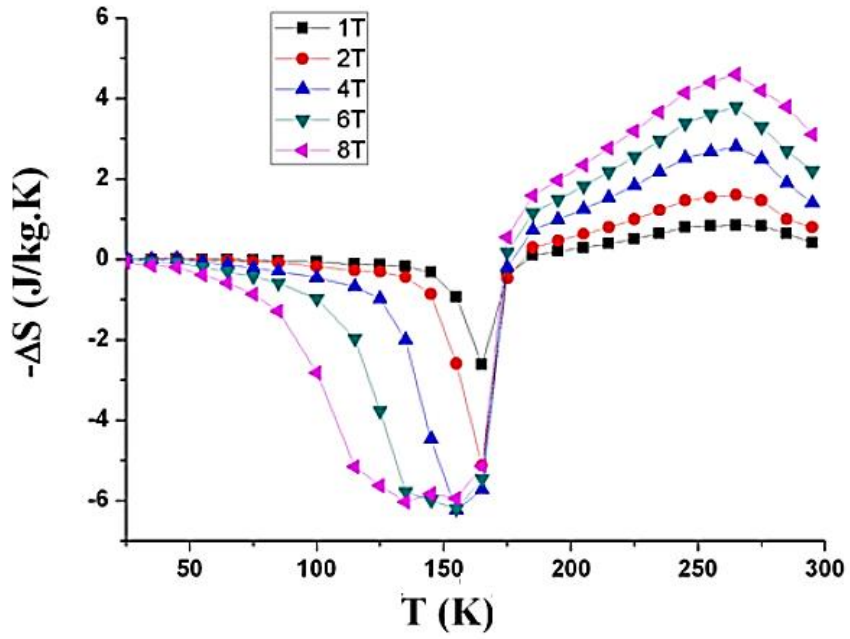

Figure 2. *Temperature dependence of magnetic entropy change under several values of applied magnetic field for $Pr_{0.5}Sr_{0.5}MnO_3$ compound*

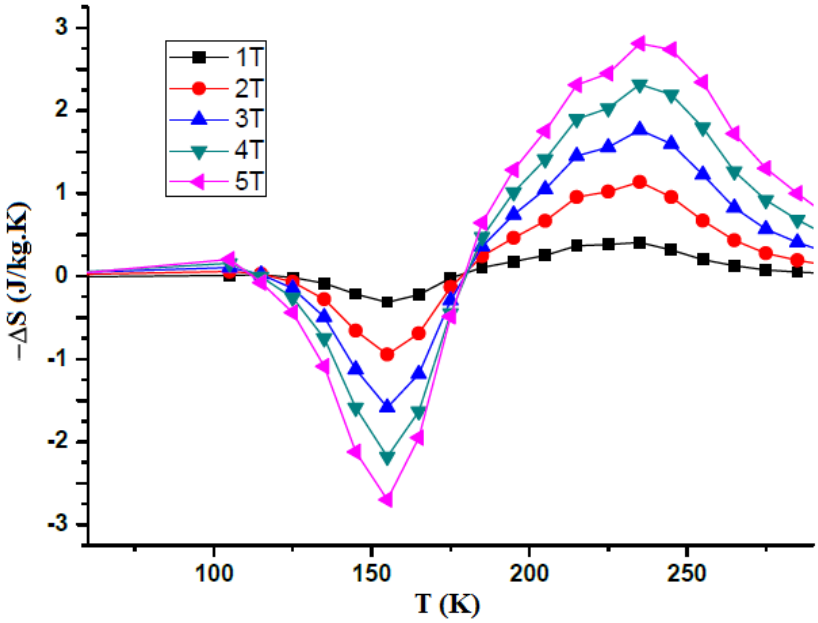

Figure 3. *Temperature dependence of magnetic entropy change under several values of applied magnetic field for $La_{0.5}Ca_{0.5}MnO_3$ compound*

Near the Curie point and under 2 T applied magnetic field, we have recorded RCP values around 126.4 J/kg and 67.8 J/kg for $Pr_{0.5}Sr_{0.5}MnO_3$ and $La_{0.5}Ca_{0.5}MnO_3$, respectively. Near the antiferromagnetic-ferromagnetic transition and under the same field value, RCP = 80.9 J/kg at T_N for $Pr_{0.5}Sr_{0.5}MnO_3$ compound and RCP = 25.5 J/kg at T_{CO} for $La_{0.5}Ca_{0.5}MnO_3$ compound. The low RCP value recorded at T_{CO} for $La_{0.5}Ca_{0.5}MnO_3$ sample can be ascribed to the phase-separated nature of this compound. Thus, magnetic phase separation phenomenon leads to the reduction of the

inverse MCE. In our case, the best magnetocaloric results were recorded for $Pr_{0.5}Sr_{0.5}MnO_3$ compound, which means that this compound is a suitable candidate for magnetic refrigeration.

4. Conclusion

In this work, we have investigated the magnetic and magnetocaloric response of two half-doped manganites $Pr_{0.5}Sr_{0.5}MnO_3$ and $La_{0.5}Ca_{0.5}MnO_3$. The magnetic study indicated that each sample possesses two different magnetic transitions as a function of temperature. The magnetocaloric study revealed the presence of both direct and inverse MCE for both samples. The best MCE was recorded in the case of $Pr_{0.5}Sr_{0.5}MnO_3$ compound.

Bibliographie

[BOU 17] BOUROUINA M., KRICHENE A., CHNIBA BOUDJADA N., KHITOUNI M., BOUJELBEN W., « Structural, magnetic and magnetocaloric properties of nanostructured $Pr_{0.5}Sr_{0.5}MnO_3$ manganite synthesized by mechanical alloying», *Ceram. Int.*, 43, p. 8139-8145, 2017.

[DAM 98] DAMAY F., MARTIN C., HERVIEU M., MAIGNAN A., RAVEAU B., ANDRÉ G., BOURÉE F., « Structural transitions in the manganite $Pr_{0.5}Sr_{0.5}MnO_3$», *J. Magn. Magn. Mater.*, 84, p. 71-82, 1998.

[DHI 20] DHIEB S., KRICHENE A., CHNIBA BOUDJADA N., BOUJELBEN W., « Suppression of metamagnetic transitions of martensitic type by particle size reduction in charge ordered $La_{0.5}Ca_{0.5}MnO_3$», *J. Phys. Chem. C*, 32, p. 17762-17771, 2020.

[DHI 23] DHIEB S., KRICHENE A., FETTAR F., CHNIBA BOUDJADA N., BOUJELBEN W., « Low temperature cluster glass behavior in nanosized $La_{0.5-x}Ho_xCa_{0.5}MnO_3$ ($0 \leq x \leq 0.15$) manganites», *J. Solid State Chem.*, 322, p. 123967, 2023.

[KRI 13] KRICHENE A., BOUJELBEN W., CHEIKHROUHOU A., « Structural, Magnetic and magnetocaloric properties in $La_{0.5-x}Re_xCa_{0.5}MnO_3$ manganites (x = 0; 0.1 and Re = Gd, Eu and Dy)», *J. Alloy. Compd.*, 550, p. 75-82, 2013.

[KRI 14] KRICHENE A., BOUJELBEN W., CHEIKHROUHOU A., « Quenching effects on correlation between electrical and magnetic properties in $Pr_{0.5}Sr_{0.5}MnO_3$ polycrystalline manganites», *Physica B*, 433, p. 122-126, 2014.

[KRI 15] KRICHENE A., SOLANKI P.S., RAYAPROL S., GANESAN V., BOUJELBEN W., KUBERKAR D.G., « B-site bismuth doping effect on structural, magnetic and magnetotransport properties of $La_{0.5}Ca_{0.5}Mn_{1-x}Bi_xO_3$», *Ceram. Int.*, 41, p. 2637-2647, 2015.

[KRI 19] KRICHENE A., BOUJELBEN W., MUKHERJEE S., SHAH N.A., SOLANKI P.S., « Magnetic phase separation in polycrystalline $Pr_{0.5-x}Bi_xSr_{0.5}MnO_3$ ($x \leq 0.15$)», *Ceram. Int.*, 45, p. 3849-3856, 2019.

[SCH 95] SCHIFFER P.E., RAMIREZ A.P., BAO W., CHEONG S.W., « Low temperature magnetoresistance and the magnetic phase diagram of $La_{1-x}Ca_xMnO_3$», *Phys. Rev. Lett.*, 75, p. 3336-3339, 1995.