Improved magnetocaloric effect in composites based on $Pr_{0.63}A_{0.07}Sr_{0.3}MnO_3$ (A = Pr, Sm and Bi) manganites

Amélioration de l'effet magnétocalorique dans des composites basés sur les manganites $Pr_{0,63}A_{0,07}Sr_{0,3}MnO_3$ (A = Pr, Sm and Bi)

Ayman Elghoul[1], Akram Krichene[2], Wahiba Boujelben[3]

[1] Laboratoire de Physique des Matériaux, Faculté des Sciences de Sfax, Université de Sfax, B.P. 1171, 3000 Sfax, Tunisia, aymenphysique3@gmail.com
[2] Laboratoire de Physique des Matériaux, Faculté des Sciences de Sfax, Université de Sfax, B.P. 1171, 3000 Sfax, Tunisia, akramkri@hotmail.fr
[3] Laboratoire de Physique des Matériaux, Faculté des Sciences de Sfax, Université de Sfax, B.P. 1171, 3000 Sfax, Tunisia, wahibaboujelben@yahoo.fr

ABSTRACT. In this work, we have investigated the magnetic and the magnetocaloric properties of polycrystalline $Pr_{0.63}A_{0.07}Sr_{0.3}MnO_3$ (A = Pr, Sm and Bi) prepared by solid-state reaction at high temperature. The magnetic study revealed that all our samples exhibit a ferromagnetic-paramagnetic transition with increasing temperature, with an important magnetocaloric effect near T_C. Using theoretical calculations, we have enhanced the magnetocaloric effect for our samples, based on theoretical composites. The obtained composites exhibit important magnetocaloric effect in an extended temperature range, which indicates the possibility of using these composites for magnetic refrigeration.

RÉSUMÉ. Dans ce travail, nous avons investigué les propriétés magnétiques et magnétocaloriques des composés polycristallins $Pr_{0,63}A_{0,07}Sr_{0,3}MnO_3$ (A = Pr, Sm et Bi) préparés par la méthode céramique à haute température. L'étude magnétique montre que nos composés montrent une transition ferromagnétique-paramagnétique lorsque la température augmente, avec un effet magnétocalorique important au voisinage de T_C. En utilisant des calculs théoriques, nous avons pu améliorer l'effet magnétocalorique pour nos composés en se basant sur des composites théoriques. Les composites obtenus montrent un effet magnétocalorique important sur une large gamme de température, ce qui indique la possibilité d'utiliser ces composites pour la réfrigération magnétique.

KEYWORDS. Manganite, composite, magnetic entropy change, magnetocaloric effect.
MOTS-CLÉS. Manganite, composite, variation d'entropie magnétique, effet magnétocalorique.

1. Introduction

Magnetic refrigeration is an emerging cooling technology based on the magnetocaloric effect (MCE) which can be defined as a modification in sample's temperature induced by an application of magnetic field. Manganites generally exhibit relatively important MCE near their Curie temperature T_C, indicating the possibility of using these specimens for magnetic refrigeration [BOU 17, ELG 16, ELG 19, PHA 07]. Magnetic refrigeration is an ecofriendly cost effective technique, which motivates the scientific community in order to get materials with improved MCE.

Previous studies have been performed on $Pr_{0.63}A_{0.07}Sr_{0.3}MnO_3$ (A = Pr, Sm and Bi) compounds [ELG 16, ELG 17]. These studies have shown that all these samples are single phase and crystallize in the orthorhombic structure with *Pnma* space group (n° 62). Moreover, T_C decreases in the case of Sm and Bi based samples. Resistivity measurements depicted an electrical transition from the metallic to the insulator behavior with increasing temperature. It was found that both electrical and magnetic transition temperatures possess very close values, suggesting the presence of a possible electrical-magnetic correlation. The critical exponents values obtained from the critical study were consistent with the tricritical mean field model for all our studied samples [ELG 17].

It is possible to enhance the MCE by gathering two or more magnetic specimens, giving birth to a composite with improved MCE [HAS 87]. In this communication, we have tried to improve the magnetocaloric properties of $Pr_{0.63}A_{0.07}Sr_{0.3}MnO_3$ (A=Pr, Sm and Bi) compounds by using theoretical composites.

2. Experimental techniques

Our samples were elaborated by using solid state reaction at high temperature by mixing high purity precursors. The details of the samples preparation were described elsewhere [ELG 16]. Magnetization measurements versus magnetic applied field up to 10 T in the temperature range 5-330 K were recorded by using a vibrating sample magnetometer.

3. Results and discussions

The temperature dependent magnetization under 0.05 T applied magnetic field is shown in figure 1. All our samples show a magnetic transition from ferromagnetic state to paramagnetic state as the temperature increases. The obtained T_C values (deduced from the minimum of dM/dT curves) are 266 K, 256 K and 211 K for our compounds substituted by Pr, Bi and Sm, respectively.

The magnetic entropy change (ΔS) was deduced from isothermal magnetization measurements according to 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.

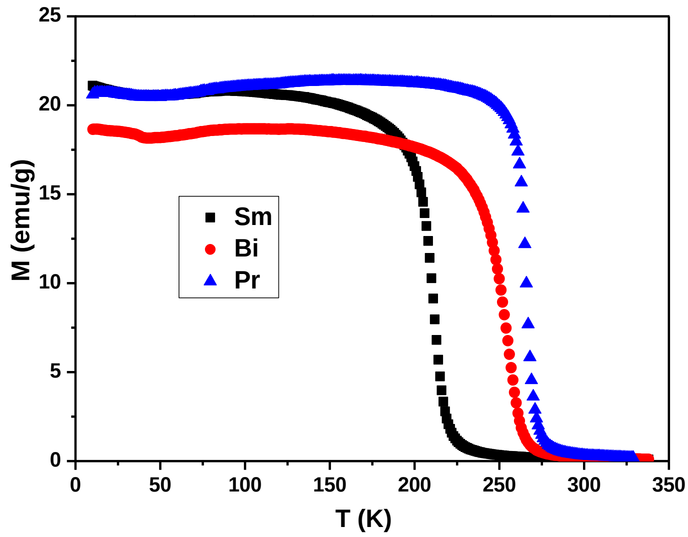

Figure 1. *Temperature dependence of magnetization under 0.05 T applied magnetic field for $Pr_{0.63}A_{0.07}Sr_{0.3}MnO_3$ (A = Pr, Sm and Bi) samples*

We have shown in figure 2 the variations of (-ΔS) as a function of the temperature under applied magnetic fields of 1 T and 2 T for the $Pr_{0.63}A_{0.07}Sr_{0.3}MnO_3$ (A=Pr, Sm and Bi) compounds. These curves show a peak around T_C, which increases with increasing the value of the applied field. All the samples demonstrate a remarkable MCE in the temperature range 180-300 K.

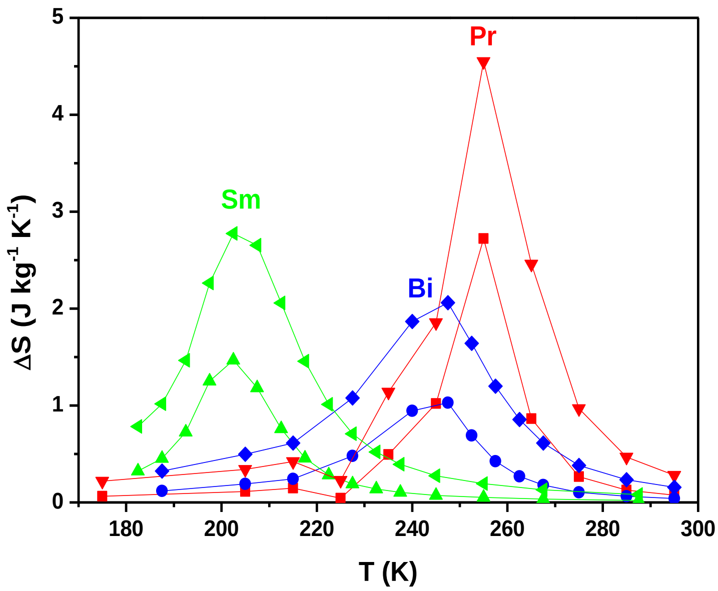

Figure 2. *Magnetic entropy change as a function of temperature under applied magnetic fields of 1 T and 2 T for $Pr_{0.63}A_{0.07}Sr_{0.3}MnO_3$ (A=Pr, Sm and Bi) samples.*

In order to evaluate the MCE, we can calculate the relative cooling power (RCP) using the following relation:

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

where δT_{FWHM} is the full width at half maximum of the magnetic entropy change curve and ΔS_{Max} is the maximum value of magnetic entropy change. All the magnetocaloric results for 2 T applied field are gathered in table 1. One can notice from table 1 the important values of ΔS_{Max} for all our samples. Besides, all our compounds exhibit an important MCE, especially the parent compound with a Curie temperature T_C = 266 K, which raises the possibility of using this compound for magnetic refrigeration.

sample	T_C (K)	$-\Delta S_{Max}$ (J/kg.K)	δ_{TFWHM} (K)	RCP (J/kg)
Pr	266	4.59	19.39	89.00
Sm	211	3.20	26.31	84.20
Bi	256	2.28	33.54	76.47

Table 1. *The values of T_C, $-\Delta S_{Max}$, δT_{FWHM} and RCP under 2 T applied field for $Pr_{0.63}A_{0.07}Sr_{0.3}MnO_3$ (A=Pr, Sm and Bi) samples*

In order to improve the MCE of our samples, it is possible to increase the RCP values by increasing δ_{FWHM} [HAS 87]. Thus, we have tried to compute the theoretical compositions for composite materials with important MCE. In this study, we have chosen four different theoretical composites. The first one is based on $Pr_{0.7}Sr_{0.3}MnO_3$ and $Pr_{0.63}Bi_{0.07}Sr_{0.3}MnO_3$ samples (Pr-Bi), the second is based on $Pr_{0.7}Sr_{0.3}MnO_3$ and $Pr_{0.63}Sm_{0.07}Sr_{0.3}MnO_3$ samples (Pr-Sm), the third one is based on $Pr_{0.63}Bi_{0.07}Sr_{0.3}MnO_3$ and $Pr_{0.63}Sm_{0.07}Sr_{0.3}MnO_3$ samples (Bi-Sm) and the fourth is a mixture of the three compounds based on Pr, Bi and Sm elements (Pr-Bi-Sm). For a refrigerant composed of n magnetocaloric phases with respective weight fraction y_1, y_2,..y_n and respective Curie temperatures Tc_1, Tc_2,… Tc_n, the ΔS values for the composite (ΔS_{com}) can be expressed as:

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$$\Delta S_{com} = \sum_i y_i \Delta S_i \qquad [3]$$

with ΔS_i is the magnetic entropy change of the sample i. For an ideal composite, the variation of ΔScom must remain constant over the refrigeration temperature range. Thus,we should resolve the following system:

$$\begin{pmatrix} \alpha_{11} & \alpha_{12} & \alpha_{13} \\ \alpha_{21} & \alpha_{22} & \alpha_{23} \\ 1 & 1 & 1 \end{pmatrix} \begin{pmatrix} y_1 \\ y_2 \\ y_3 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix} \qquad [4]$$

and the α_{ij} coefficients can be evaluated according to the relation:

$$\alpha_{ij} = \Delta S_j(T_C^{i+1}) - \Delta S_j(T_C^{i}) \qquad [5]$$

The y_i values for our composites are gathered in table 2. Based on the results of table 2, we have shown in figure 3 the evolution of ($-\Delta S_{com}$) versus temperature under a magnetic applied field of 2 T for all the calculated the composites. We have listed in table 3 the values of Tc, $-\Delta S_{com}^{Max}$, δT_{FWHM} and RCP for our theoretical composites under a magnetic applied field of 2T.

composite	Pr-Bi	Pr-Sm	Bi-Sm	Pr-Bi-Sm
yPr (%)	21.86	41.69	-	15.26
yBi (%)	78.14	-	62.38	36.67
ySm (%)	-	58.31	37.62	48.07

Table 2. *Theoretical compositions for all the studied composites*

sample	T_C (K)	$-\Delta S_{Max}$ (J/kg.K)	δ_{TFWHM} (K)	RCP (J/kg)
Pr-Bi	243	2.31	37.42	86.18
Pr-Sm	222	3.51	25.60	89.81
Bi-Sm	230	2.51	32.63	81.92
Pr-Bi-Sm	224	2.79	30.66	85.60

Table 3. *T_C, ΔS_{Max}, δT_{FWHM} and RCP for our studied composites under a magnetic applied field of 2T*

We can observe that the maximum values of ΔS are reduced compared to the other samples (table 1). However, it is possible to notice an enhancement in the RCP values because the composites are active in a large temperature range. Such behavior is generally observed for manganite-based composites [ELG 18, JER 15, KRI 18]. Therefore, the theoretical composites are characterized by improved MCE, which indicates the importance of the theoretical calculation. The best results were obtained for Pr-Sm composite. Besides, one can observe that Pr-Bi composite have the highest T_C with a plateau-like shape of ΔS(T) curve, leading to a stable MCE in a large temperature range. Thus, these composites can be used in the magnetic refrigeration field.

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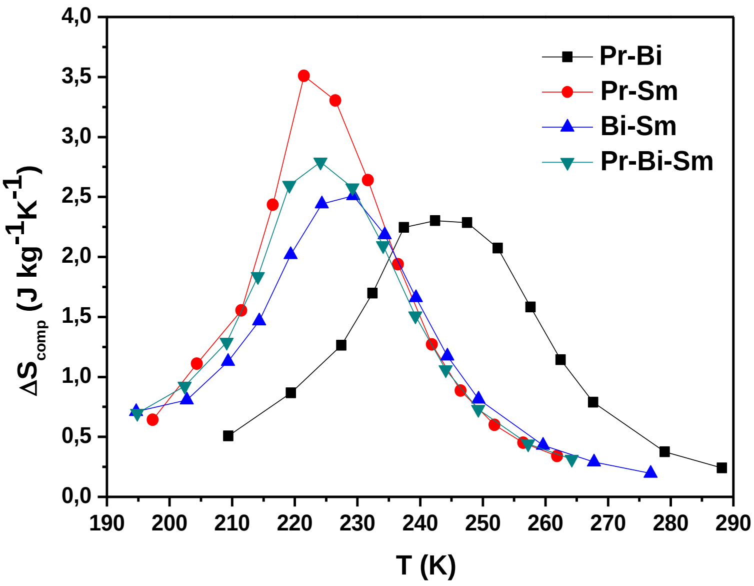

Figure 3. *Theoretical entropy as a function of temperature for all the calculated composites*

4. Conclusion

In this paper, we have tried to improve the magnetocaloric properties of $Pr_{0.63}A_{0.07}Sr_{0.3}MnO_3$ (A = Pr, Sm and Bi) compounds by using theoretical calculations in order to obtain theoretical composites. Important values of MCE were recorded for Pr-Sm and Pr-Bi composites, indicating the possibility of using these composites for magnetic refrigeration.

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