

A comparative study of the structural, magnetic and magnetocaloric properties in $\text{Pr}_{0.6}\text{La}_{0.1}\text{M}_{0.3}\text{MnO}_3$ manganites ($\text{M} = \text{Ca}, \text{Ba}$ and Mg)

S. Zouari¹, E. K. Hlil², M. L. Kahn³, M. Ellouze¹ and F. Elhalouani⁴

¹ LMF, University of Sfax, Faculty of Sciences of Sfax, B. P. 1171 - 3000, Tunisia

² Institut Néel, CNRS et Université Joseph Fourier, BP 166, F -38042 Grenoble Cedex 9, France

³ Laboratory of Chemical of Coordination (LCC) of CNRS, University Paul Sabatier, BP 44099, F -31077, Toulouse, Cedex 4, France

⁴ National Engineering School of Sfax, B. P. W - 3038, Tunisia

*Corresponding author: Sana Zouari email: Zouari_sana85@yahoo.fr

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Abstract

The Comparison of the structural, magnetic and magnetocaloric properties of $\text{Pr}_{0.6}\text{La}_{0.1}\text{M}_{0.3}\text{MnO}_3$ ($\text{M} = \text{Ca}, \text{Ba}$ and Mg) compounds have been studied using X-ray diffraction (XRD) and magnetic measurements. Our compounds have been prepared using the Sol-Gel method reaction at room temperature. Rietveld refinements of the X-ray diffraction patterns reveal that our compounds are single phase and crystallize in the orthorhombic system with $Pnma$ space group. Magnetization measurements versus temperature in a magnetic applied field of 0.05T indicate that samples display a ferromagnetic (FM) - paramagnetic (PM) transition with increasing temperature. The Curie temperature T_c is found to be 94 K, 39 K and 64 K for $\text{M} = \text{Ca}, \text{Ba}$ and Mg , respectively. From the magnetization data as a function of magnetic applied field, we have determined the associated magnetic entropy change, the maximum of the magnetic entropy $|\Delta S_M^{\text{Max}}|$ and the relative cooling power (RCP) for $\text{Pr}_{0.6}\text{La}_{0.1}\text{M}_{0.3}\text{MnO}_3$ ($\text{M} = \text{Ca}, \text{Ba}$ and Mg) compounds. In the vicinity of T_c and in a magnetic applied field of 2 T, $|\Delta S_M^{\text{Max}}|$ reached, the values of 0.87 J/kg K, 1.43 J/kg K and 0.79 J/kg K for $\text{M} = \text{Ca}, \text{Ba}$ and Mg , respectively.

Key words: sol-gel, X-ray diffraction, Magnetic properties, Magnetocaloric effect.

Introduction

Mixed valence manganese oxides $\text{Ln}_{1-x}\text{A}_x\text{MnO}_3$ (Ln = rare-earth, A = alkali metal or alkaline-earth) with perovskite structure are the topic of continuing interest for various decades. This interest appears from their fascinating magnetic performance and transport properties, as well as practical applications [1, 2]. In these compounds, double exchange interactions and the limited lattice distortions, starting from Jahn-Teller effect, have been implored to clarify the magneto-transport properties [3, 4]. Now, magnetic refrigeration is enhancing hopeful technology to modify the conventional gas-compression expansion technique [5]. The magnetocaloric effect (MCE) is a subject property of a magnetic material appears due to the coupling of

magnetic sub-lattice with the magnetic field. With the aim of achieving large magnetic entropy changes induced costs, by the low tunable magnetic field changes at low temperature, many researchers have revealed that Curie temperature as well as magnetic entropy change can be tuned by controlling relative ratio $\text{Mn}^{3+}/\text{Mn}^{4+}$ [6], the average size of the $\langle r_A \rangle$ cation site [7]. Our present study has been carried out to study the effect of Ca, Ba and Mg substitution on the magnetic and magnetocaloric properties of $\text{Pr}_{0.6}\text{La}_{0.1}\text{M}_{0.3}\text{MnO}_3$ ($\text{M} = \text{Ca}, \text{Ba}$ and Mg) compounds. These samples, with fixed $\text{Mn}^{3+}/\text{Mn}^{4+}$ ratio, and various $\langle r_A \rangle$ values, provide a good system to detect the individual magnetic nature of rare earth ion in perovskite manganites.

2. Experimental techniques

$\text{Pr}_{0.6}\text{La}_{0.1}\text{M}_{0.3}\text{MnO}_3$ ($\text{M} = \text{Ca}, \text{Ba}$ and Mg) compounds have been prepared using the Sol-Gel method at room temperature. Stoichiometric amounts of Pr_2O_3 , La_2O_3 , BaO , CaO , MgO and Mn_2O_3 were dissolved in nitric acid, HNO_3 . Suitable amounts of

citric acid and ethylene glycol as coordinate agent were added with respect to the compounds formation and a complete homogenous transparent solution was obtained. Finally, the resulted precursor was annealed in air at 1000°C for 3 hours.

Phase purity, homogeneity and cell dimensions were checked by powder X-ray diffraction at room temperature. Structural analysis was carried out using the standard Rietveld technique using the FULLPROF program [8, 9]. Magnetization measurements versus

temperature in the range 0–200 K were carried out using a SQUID magnetometer. MCE was deduced from the magnetization measurements versus magnetic applied from 0 to 5T at several temperatures around the Curie temperature (T_c).

3. Results and discussion

3.1. Structural properties

The $\text{Pr}_{0.6}\text{La}_{0.1}\text{M}_{0.3}\text{MnO}_3$ ($M = \text{Ca}, \text{Ba}$ and Mg) compounds were characterized by the X-ray powder diffraction (XRD) patterns at room temperature [10–12]. All reflection lines were successfully indexed according to the orthorhombic perovskite structure with $Pnma$

space group. The unit cell volume and the lattice parameters obtained by whole patterns refinements are given in Table 1.

Table. 1 Lattice parameters, unit cell volume, magnetic properties and grain size (D) of $\text{Pr}_{0.6}\text{La}_{0.1}\text{M}_{0.3}\text{MnO}_3$ ($M = \text{Ca}, \text{Ba}$ and Mg) compounds.

$\text{Pr}_{0.6}\text{La}_{0.1}\text{M}_{0.3}\text{MnO}_3$	a (Å)	b (Å)	c (Å)	V (Å ³)	D	T_c (K)
M = Ca	5.4549 ₁	7.6861 ₂	5.4415 ₃	228.14 ₈	37.05	94
M = Ba	5.4315 ₆	7.6476 ₁	5.4173 ₇	225.03	28	39
M = Mg	5.4856	7.7348	5.4760	232.35 ₁	29.28	64

The unit cell volume decreases with $\langle r_c \rangle$ increasing (Table. 2). This behavior is due to the difference ionic radius of Ca, Ba and Mg. The tolerance factors (t_c) were estimated [13]. The calculated tolerance factors (t_c) ranges between 0.89 and 0.96 in agreement with an orthorhombic structure (Table 2). The ionic radii were taken according to Shannon [14, 15].

Table. 2 Variation of $\langle r_A \rangle$, $\langle r_M \rangle$, $\langle r_B \rangle$ and t_G for $\text{Pr}_{0.6}\text{La}_{0.1}\text{M}_{0.3}\text{MnO}_3$ ($M = \text{Ca}, \text{Ba}$ and Mg) compounds.

Compounds	$\text{Pr}_{0.6}\text{La}_{0.1}\text{M}_{0.3}\text{MnO}_3$		
	M = Mg	M = Ca	M = Ba
r_M (Å)	0.72	1.18	1.57
r_A (Å)	1.045	1.183	1.3
r_B (Å)	0.61	0.61	0.61
V (Å ³)	232.35	228.1	225.03
T_c	0.862	0.914	0.952

The average grain size (D) was estimated from the X-ray diffraction peaks using the Scherrer formula [16]: $D = \frac{K\lambda}{\beta \cos \theta}$. λ is the X-ray wavelength employed, θ is the diffraction angle for the most intense peak [17] and β is defined as $\beta^2 = \beta_m^2 - \beta_s^2$. Here, β_m is the experimental full width at half maximum (FWHM) and β_s is the FWHM of a standard silicon sample the experimental full width at half-maximum (FWHM) of the same peak. The values of the effective particle size (D) are summarized in Table 1. We conclude that the $\text{Pr}_{0.6}\text{La}_{0.1}\text{Ba}_{0.3}\text{MnO}_3$ compound has the smaller Grain size (D = 28nm).

3.2. Magnetic properties

Magnetization measurements as a function of temperature in a magnetic applied field of 0.05T prove that our synthesized compounds display a ferromagnetic to paramagnetic transition with increasing temperature (Fig. 1). The Curie temperatures (T_c) values, defined in terms of the inflection point of M (T) curve obtained using the derivative dM/dT as function of temperature are listed in Table 1. It should be observed that the magnetization decreasing at low temperature observed in $\text{Pr}_{0.6}\text{La}_{0.1}\text{Ba}_{0.3}\text{MnO}_3$ and $\text{Pr}_{0.6}\text{La}_{0.1}\text{Mg}_{0.3}\text{MnO}_3$ compounds arise from the polarization of the magnetic rare earth

ion sub-lattice influenced by the molecular field of Mn ions [18].

In order to conclude the type of magnetic phase transition in $\text{Pr}_{0.6}\text{La}_{0.1}\text{M}_{0.3}\text{MnO}_3$ (M = Ca, Ba and Mg) compounds, we have analyzed H/M versus M^2 curves extracted from the isothermal M vs. H data (Fig. 2) using Banerjee criterion [19]. According to this criterion, the magnetic transition is the first order (second order) if the slope the plot H/M is negative (positive). For our compounds, a second order phase transition has been proved from the positive slope of H/M versus M^2 curves.

3.3. Magnetocaloric effect

The total magnetic entropy $|\Delta S_M|$ as a function of temperature and magnetic applied field for our synthesized compounds were valued from magnetization isotherms. According to the thermodynamic theory based on Maxwell relations, the entropy change $|\Delta S_M|$ can be given through the formula:

$$\left(\frac{\delta M(H,T)}{\delta T}\right)_H = \left(\frac{\delta S_M(H,T)}{\delta H}\right)_T$$

which directly implies that: $\Delta S_M(T, H) = \int_0^H \left(\frac{\delta M}{\delta T}\right)_H \delta H$

The $|\Delta S_M|$ values of $\text{Pr}_{0.6}\text{La}_{0.1}\text{M}_{0.3}\text{MnO}_3$ (M = Ca, Ba and Mg) compounds for different external magnetic applied field are listed in Table.3.

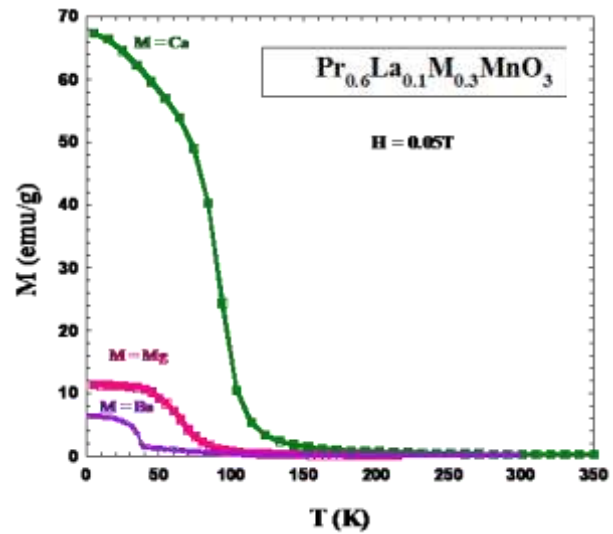


Figure 1. Temperature dependence of the magnetization at $\Delta H = 0.05\text{T}$ for $\text{Pr}_{0.6}\text{La}_{0.1}\text{M}_{0.3}\text{MnO}_3$ (M = Ca, Ba and Mg) compounds.

Table. 3 The maximum of the magnetic entropy $|\Delta S_M^{\text{Max}}|$ of $\text{Pr}_{0.6}\text{La}_{0.1}\text{M}_{0.3}\text{MnO}_3$ (M = Ca, Ba and Mg) compounds.

<i>Magnetic fields</i>	$\text{Pr}_{0.6}\text{La}_{0.1}\text{M}_{0.3}\text{MnO}_3$		
	M = Ca	M = Ba	M = Mg
	$ \Delta S_M^{\text{Max}} \text{ (J/Kg.K)}$	$ \Delta S_M^{\text{Max}} \text{ (J/Kg.K)}$	$ \Delta S_M^{\text{Max}} \text{ (J/Kg.K)}$
1 T	0.54	0.56	0.40
2 T	0.87	1.43	0.79
3 T	1.72	2.48	1.10
4 T	2.23	2.83	1.42
5 T	2.7	2.92	1.74

All our compounds reveal large MCE effect close to the Curie temperature due to the large drop in magnetization. The maximum of the magnetic entropy achieves the highest value of 1.43 J/kg K at 39 K upon a magnetic field change of 2 T for $\text{Pr}_{0.6}\text{La}_{0.1}\text{Ba}_{0.3}\text{MnO}_3$ compound. The value of $|\Delta S_M^{\text{Max}}|$ of $\text{Pr}_{0.6}\text{La}_{0.1}\text{Ba}_{0.3}\text{MnO}_3$ compound at 5T (Table3), is found to be higher than that reported recently by Kh. Sbissi et al. in $\text{Pr}_{0.8}\text{Bi}_{0.2}\text{MnO}_3$ compound ($|\Delta S_M^{\text{Max}}| = 2.77 \text{ J/kg K}$ for H = 5T at 114 K) [20].

The relative cooling power (RCP) is estimated as $\text{RCP} = -\Delta S_M^{\text{max}} \times \delta T_{\text{FWHM}}$, where δT_{FWHM} is the full width of half maximum of $|\Delta S_M^{\text{max}}|$ versus temperature [21]. The RCP values achieved upon a magnetic applied change of 2T are respectively, 68.87 J/kg, 45.49 J/kg and 38.74 J/kg at 2 T for M = Ca, Ba and Mg. In Table 3, we list the MCE values of the present compounds in comparison with those reported in the literature having similar Tc.

Compared with other materials considered as suitable for applications in magnetic refrigerators and having similar T_c , our results are interesting enough to

cover the way for investigations of materials useful as a possible refrigerant for low temperature magnetic refrigeration (Table. 4).

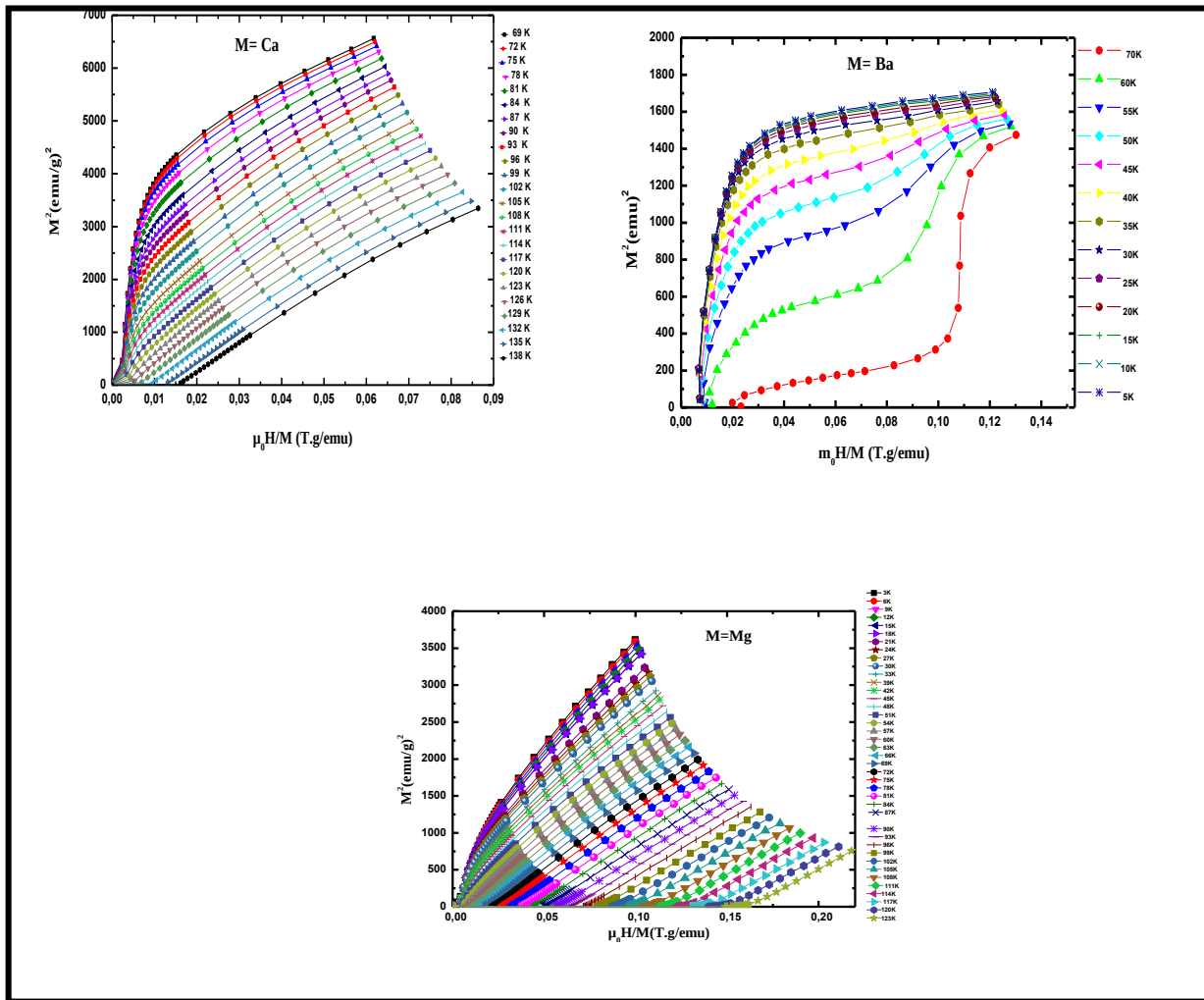


Figure 2. Arrot curves M^2 versus $\mu_0 H/M$ for $\text{Pr}_{0.6}\text{La}_{0.1}\text{M}_{0.3}\text{MnO}_3$ ($M = \text{Ca}, \text{Ba}$ and Mg) compounds.

Table. 3 The maximum of the magnetic entropy $|\Delta S_M^{\text{Max}}|$ of $\text{Pr}_{0.6}\text{La}_{0.1}\text{M}_{0.3}\text{MnO}_3$ ($M = \text{Ca}, \text{Ba}$ and Mg) compounds.

	T_c (K)	ΔH (T)	$ \Delta S_M^{\text{Max}} $ (J/Kg.K)	RCP (J.K ⁻¹)	Ref
$\text{Pr}_{0.6}\text{La}_{0.1}\text{Ca}_{0.3}\text{MnO}_3$	94	2	0.87	68.87	This work
$\text{Pr}_{0.6}\text{La}_{0.1}\text{Mg}_{0.3}\text{MnO}_3$	65	2	1.43	38.74	This work
$\text{Pr}_{0.6}\text{La}_{0.1}\text{Ba}_{0.3}\text{MnO}_3$	39	2	0.79	45.49	This work
$\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$	220	2	1.13	67.8	[22]
$\text{La}_{0.4}\text{Gd}_{0.1}\text{Ca}_{0.5}\text{MnO}_3$	100	2	0.78	67.84	[22]
$\text{Pr}_{0.8}\text{Pb}_{0.2}\text{MnO}_3$	175	1.35	2.64	55	[23]
$\text{La}_{0.62}\text{Bi}_{0.02}\text{Ca}_{0.33}\text{MnO}_3$	248	2	5.3	125	[24]
Gd	294	5	5	196	[25]

4. Conclusion

The $\text{Pr}_{0.6}\text{La}_{0.1}\text{M}_{0.3}\text{MnO}_3$ ($\text{M} = \text{Ca}, \text{Ba}$ and Mg) compounds were studied using X-ray and magnetic measurements. The structural study proves that all our synthesized compounds crystallize in the orthorhombic structure with Pnma space group. All our compounds display a FM - PM transition with temperature increasing. Large MCE has been achieved in all compounds at the Curie temperature T_c and the maximum of the magnetic entropy $|\Delta S_M^{\text{Max}}|$ acquire the

highest value of 1.43 J/kg K for the $\text{Pr}_{0.6}\text{La}_{0.1}\text{Ba}_{0.3}\text{MnO}_3$ compound upon a magnetic applied field change of 2 T. The study of the magnetocaloric effect proves that the $\text{Pr}_{0.6}\text{La}_{0.1}\text{Ca}_{0.3}\text{MnO}_3$ compound is the most important candidate for potential applications in the field of magnetic refrigeration at low temperatures. The attained RCP values of our compounds are similar with other reported values for materials used as magnetic refrigerants at low temperature.

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