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Structural, magnetic and magnetocaloric properties in $Pr_{0.5}M_{0.1}Sr_{0.4}MnO_3$ (M = Eu, Gd and Dy) polycristalline manganites

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ABSTRACT

Structural, magnetic and magnetocaloric properties of $Pr_{0.5}M_{0.1}Sr_{0.4}MnO_3$ (M = Eu, Gd and Dy) powder samples have been investigated by X-ray diffraction (XRD) and magnetic measurements. Our samples have been synthesized using the solid state reaction method at high temperature. Rietveld refinements of the X-ray diffraction patterns show that all our samples are single phase and crystallize in the distorted orthorhombic system with *Pbnm* space group. Magnetization measurements versus temperature in a magnetic applied field of 50 mT show that all our samples exhibit a paramagnetic–ferromagnetic transition with decreasing temperature. The Curie temperature T_C is found to be 270 K, 258 K and 248 K for M = Eu, Gd and Dy, respectively. Arrott plots show that all our samples exhibit a second order magnetic phase transition. From the measured magnetization data of $Pr_{0.5}M_{0.1}Sr_{0.4}MnO_3$ (M = Eu, Gd and Dy) samples as a function of magnetic applied field, the associated magnetic entropy change $|\Delta S_M|$ and the relative cooling power RCP have been determined. In the vicinity of T_C, $|\Delta S_M|$ reached, in a magnetic applied field of 1 T, maximum values of 1.37 J/kg K, 1.23 J/kg K and 1.18 J/kg K for M = Eu, Gd and Dy, respectively.

1. Introduction

Doped manganites $Ln_{1-x}A_xMnO_3$ (Ln = rare-earth, A = alkali-metal or alkaline-earth) with perovskite structure are the subject of continuing interest for several decades. This interest comes from their intriguing magnetic behavior and transport properties, as well as practical applications [1–3]. In these compounds, double exchange interactions and the localized lattice distortions, arising from Jahn–Teller effect, have been invoked to explain the magneto-transport properties [4,5]. Nowadays, magnetic refrigeration is becoming promising technology to replace the conventional gas-compression expansion technique [6,7]. The magnetocaloric effect (MCE) is an intrinsic property of a magnetic material arising due to the coupling of magnetic sub-lattice with the magnetic field. It is well known that the main requirements for a magnetic material to possess a large magnetic entropy change, $|\Delta S_M|$, are the large spontaneous magnetization as well as the sharp drop in the magnetization associated with the ferromagnetic to paramagnetic transition at the Curie temperature [8–10]. Compared with gadolinium ($|\Delta S_M^{Max}| = 10.2$ J/kg K for $\Delta H = 5$ T at 294 K) [10] and $Gd_5Si_2Ge_2$ alloy ($|\Delta S_M^{Max}| = 18.4$ J/kg K for $\Delta H = 5$ T at 276 K) [11] which are considered as the most active materials for applications as working substance for magneto-refrigerant around room temperature; manganites and despite their lower $|\Delta S_M^{Max}|$ values, present several advantages. In fact, the low production costs, the tunable T_C, the chemical stability and the higher resistivity which is favorable for reducing eddy current heating, make these compounds potential candidates for magnetic refrigeration. In order to attain large magnetic entropy changes induced by low magnetic field changes at room temperature, many researchers have shown that Curie temperature as well as magnetic entropy change can be tuned by controlling the relative ratio Mn^{3+}/Mn^{4+} [12], the average size of the A cation site $\langle r_A \rangle$ [13] and the disorder degree of the so-called mismatch A site effect given by $\sigma^2 = \sum y_i r_i^2 - \langle r_A \rangle^2$ (y_i: fractional occupancy) [14]. The results of magnetic and transport properties reported on $La_{0.7-x}Ln_xSr_{0.3}MnO_3$ (Ln = Sm, Gd and Dy) show that with decreasing $\langle r_A \rangle$, the ferromagnetic transition temperature shifts to lower values and both values of resistivity and magnetoresistance ratio increase [15]. These authors explained their results by the influence of the magnetism of substitution ions on the Mn–O layers.

Our present study has been carried out to investigate the effect of Eu, Gd and Dy substitution on the magnetic and magnetocaloric

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Table 1
Refined structural parameters of $Pr_{0.5}M_{0.1}Sr_{0.4}MnO_3$ (M = Eu, Gd and Dy) at room temperature.

	M = Eu	M = Gd	M = Dy
a (Å)	5.443(1)	5.441(1)	5.441(2)
b (Å)	5.472(2)	5.469(9)	5.468(1)
c (Å)	7.681(8)	7.679(2)	7.678(6)
V (Å^3)	228.81	228.54	228.45
Mn–O1 (Å)	1.965(1)	1.956(1)	1.951(1)
Mn–O2 (Å)	1.940(1)	1.920(1)	1.920(1)
Mn–O2 (Å)	1.950(1)	1.970(1)	1.905(1)
Mn–O1–Mn (°)	166.0(1)	157.8(1)	159.4(1)
Mn–O2–Mn (°)	155.5(1)	165.1(3)	163.1(1)
t	0.9287	0.9282	0.9274
$\langle r_A \rangle$ (Å)	1.225	1.224	1.221
σ^2 (Å^2)	50.5×10^{-4}	53.3×10^{-4}	59.5×10^{-4}
χ^2	1.21	1.39	1.38

properties of $Pr_{0.5}M_{0.1}Sr_{0.4}MnO_3$ (M = Eu, Gd and Dy) powder samples. Our doped samples, characterized approximately by fixed Mn^{3+}/Mn^{4+} ratio, $\langle r_A \rangle$ and σ^2, provide a good system to detect the individual magnetic nature of rare earth ion in perovskite manganites.

2. Experimental techniques

Powder samples of $Pr_{0.5}M_{0.1}Sr_{0.4}MnO_3$ (M = Eu, Gd and Dy) have been synthesized using the standard solid state reaction method at high temperature. The starting materials were intimately mixed in an agate mortar and then heated in air up to 1000 °C for 60 h. The obtained powders were then pressed into pellets (of about 1 mm thickness and 13 mm diameter) and sintered at 1100 °C in air for 60 h with intermediate regrinding and repelling. Finally, these pellets were rapidly quenched to room temperature in air in order to freeze the structure at the annealed temperature. Phase purity, homogeneity and cell dimensions were determined by powder X-ray diffraction at room temperature. As our samples have been synthesized in air, they are consequently stoichiometric in oxygen [16]. Structural analysis was carried out using the standard Rietveld technique [17,18]. The amount of Mn^{4+} ions has been quantitatively checked by iodometric titration. Magnetization measurements versus temperature in the range 5–300 K and versus magnetic applied field up to 8 T were carried out using a vibrating sample magnetometer. MCE were deduced from the magnetization measurements versus magnetic applied field up to 8 T at several temperatures.

3. Results and discussion

The X-ray powder diffraction (XRD) patterns at room temperature for the $Pr_{0.5}M_{0.1}Sr_{0.4}MnO_3$ (M = Eu, Gd and Dy) samples are shown in Fig. 1. It has been found that all our samples can be indexed in the orthorhombic system with *Pbnm* space group. The final refinement values of the structural parameters and χ^2 values of the Rietveld analysis are summarized in Table 1. In this table the tolerance factor (t), the average size of A-site cations ($\langle r_A \rangle$) and the mismatch size (σ^2) at the A-site are also listed. The ionic radii were taken according to Shannon [19]. The lattice parameters a, b and $c/\sqrt{2}$ verified the relation $c/\sqrt{2} < a < b$ which indicates that the samples are characterized by the presence of the static Jahn–Teller distortion. One can observe that there is no significant change of the unit cell volume since Mn^{3+}/Mn^{4+} ratio, $\langle r_A \rangle$ and σ^2 are approximately constant.

Magnetization measurements as a function of temperature in the range 5–300 K and in a magnetic applied field of 50 mT showed that our synthesized samples exhibit a paramagnetic to ferromagnetic transition with decreasing temperature (Fig. 2a). The Curie temperature T_C, determined from the position of the inflexion point in the $M(T)$ curve, is found to be 270 K, 258 K and 248 K for M = Eu, Gd and Dy, respectively. It should be noted that the magnetization increase at low temperature observed in M = Gd and Dy samples arise from the polarization of the magnetic rare earth ion sublattice induced by the molecular field of Mn ions [20]. For all our samples, in the paramagnetic phase ($T > T_C$), the temperature dependence of the magnetic susceptibility follows the Curie–Weiss law, $\chi = C/(T - \theta_P)$, where C is the Curie constant and θ_P is the Curie–Weiss temperature. The values of θ_P are found to be 255 K, 239 K and 232 K for M = Eu, Gd and Dy, respectively. The positive θ_P values imply the ferromagnetic nature of the magnetic interactions between Mn ions. The Curie constant values calculated from the line slopes of the reciprocal susceptibility versus temperature curve, $\chi^{-1}(T)$, have been used to estimate the experimental effective paramagnetic moment $\mu_{\text{eff}}^{\text{exp}}$. $\mu_{\text{eff}}^{\text{exp}}$ values are found to be 5.17 μ_B, 5.75 μ_B and 6.17 μ_B for M = Eu, Gd and Dy, respectively.

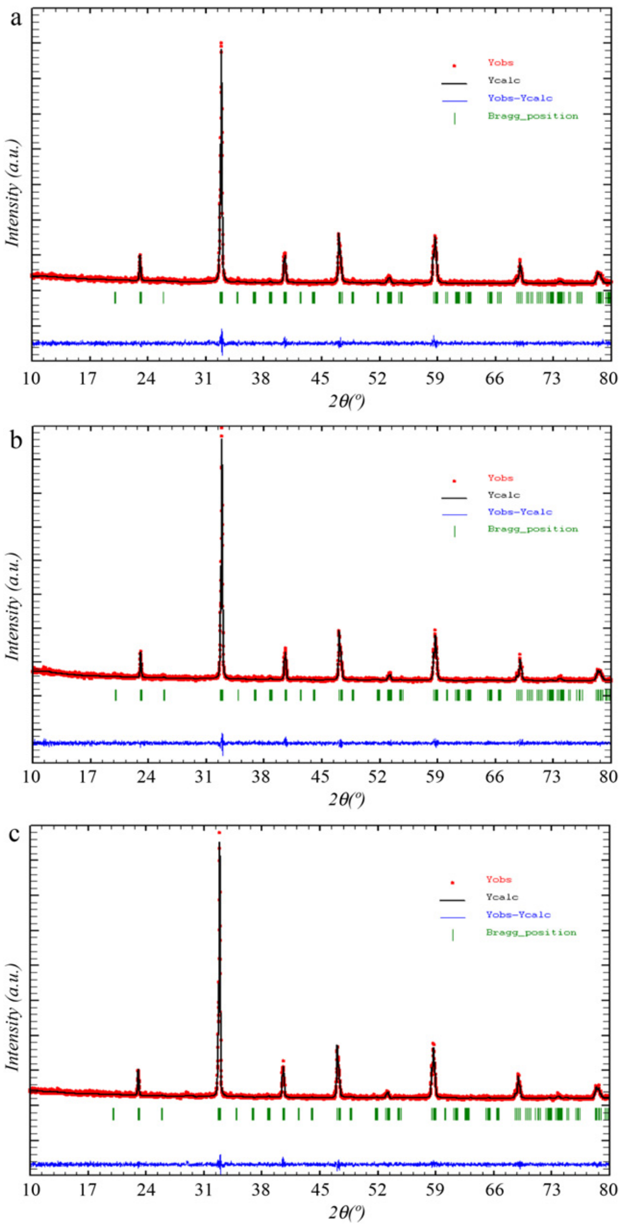

Fig. 1. XRD patterns of (a) $Pr_{0.5}Eu_{0.1}Sr_{0.4}MnO_3$, (b) $Pr_{0.5}Gd_{0.1}Sr_{0.4}MnO_3$ and (c) $Pr_{0.5}Dy_{0.1}Sr_{0.4}MnO_3$ compounds. Squares indicate the experimental data and the calculated data is the continuous line overlapping them. The lowest curve shows the difference between experimental and calculated patterns. The vertical bars indicate the expected reflection positions.

Fig. 2b shows the magnetization measurements versus magnetic applied field up to 8 T of $Pr_{0.5}M_{0.1}Sr_{0.4}MnO_3$ (M = Eu, Gd and Dy) samples at low temperature (T = 20 K). For $Pr_{0.5}Eu_{0.1}Sr_{0.4}MnO_3$ sample, the magnetization reaches saturation at about 0.8 T. The experimental value of the spontaneous magnetization, $M_{\text{sp(exp)}}$, is

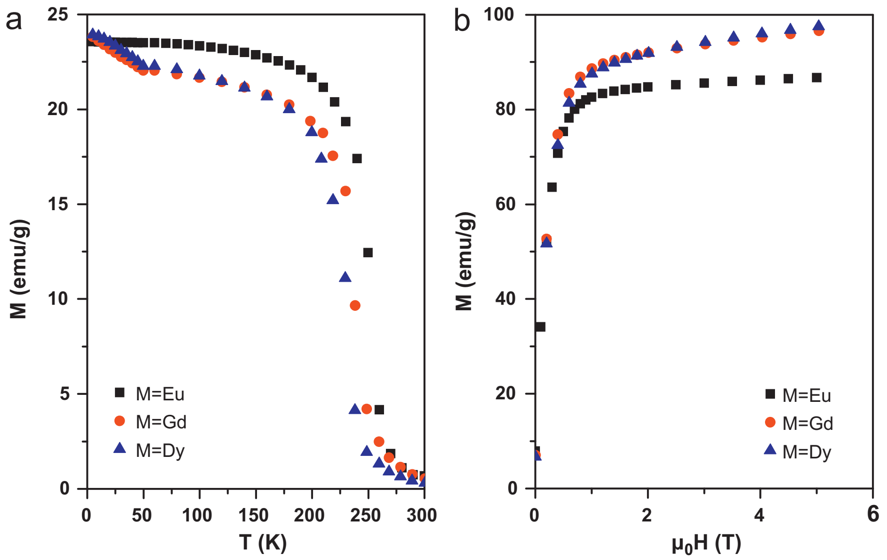

Fig. 2. (a) Temperature dependence of the magnetization at $\mu_0 H$ = 50 mT for $Pr_{0.5}M_{0.1}Sr_{0.4}MnO_3$ (M = Eu, Gd and Dy) compounds. (b) Magnetization evolution versus magnetic applied field up to 7 T at 20 K for $Pr_{0.5}M_{0.1}Sr_{0.4}MnO_3$ (M = Eu, Gd and Dy) compounds.

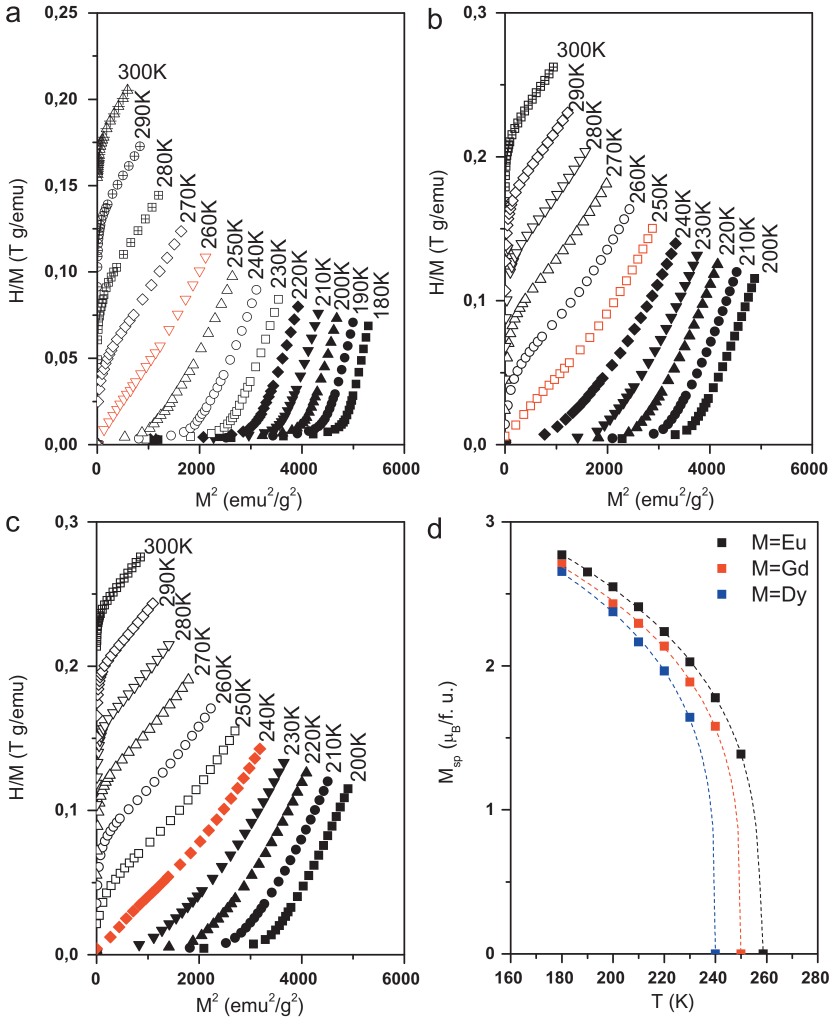

Fig. 3. H/M versus M^2 isotherms for $Pr_{0.5}M_{0.1}Sr_{0.4}MnO_3$ samples around their respective Curie temperature (a) M = Eu, (b) M = Gd, (c) M = Dy (the red lines indicates the Curie temperature) and (d) the spontaneous magnetization (M_{sp}) as a function of temperature for $Pr_{0.5}M_{0.1}Sr_{0.4}MnO_3$ (M = Eu, Gd and Dy) compounds along with the fit obtained with the help of the power law. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

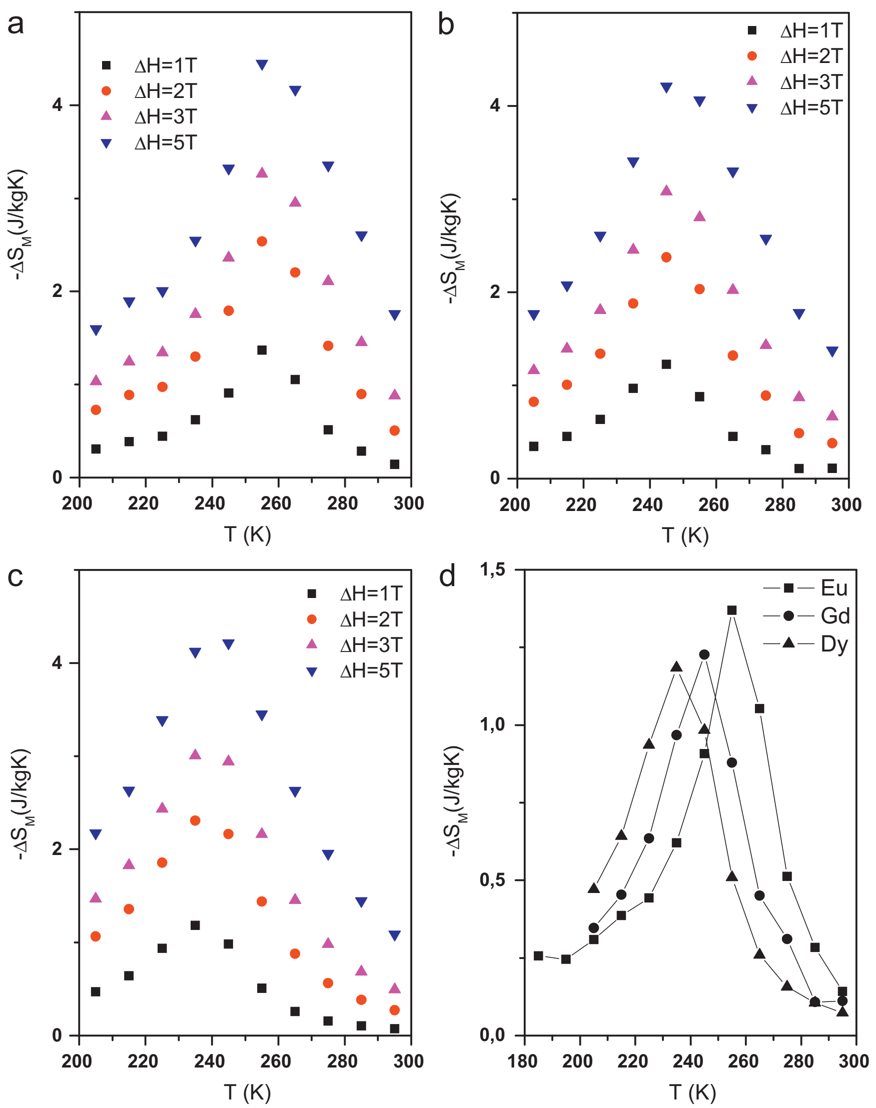

Fig. 4. Magnetic entropy change $|\Delta S_M|$ as a function of temperature at several magnetic applied fields for $Pr_{0.5}M_{0.1}Sr_{0.4}MnO_3$ samples (a) M = Eu, (b) M = Gd, (c) M = Dy and (d) $|\Delta S_M|$ versus temperature upon a magnetic field change of 1 T for $Pr_{0.5}M_{0.1}Sr_{0.4}MnO_3$ (M = Eu, Gd and Dy) compounds.

found to be 3.47 μ_B/Mn which is slightly lower than the theoretical value of 3.6 μ_B/Mn, obtained for full spin alignment of the Mn magnetic moments. For M = Gd and Dy samples, there exists a small slope in the $M(H)$ curve at high field, the saturation magnetization is not achieved even at 5 T. These results can be attributed to the magnetic moment of rare earth ions at A-site.

For all our samples, Arrott plots above T_C show a linear behavior which indicates that a second order magnetic transition occurs [21]. We plot in Fig. 3d the temperature dependence of the spontaneous magnetization along with the fit obtained using $M_{sp}(T) = M_{sp}(0)[1-(T/T_C)]^{\gamma}$. This plot allowed an estimation of the critical exponent γ, which is found to be 0.30, 0.28 and 0.27 for M = Eu, Gd and Dy, respectively.

Table 2
The relative cooling power of $Pr_{0.5}M_{0.1}Sr_{0.4}MnO_3$ (M = Eu, Gd and Dy) samples.

	RCP (J/kg)		
	M = Eu	M = Gd	M = Dy
1 T	47.93	46.02	48.29
2 T	112.04	113.91	119.76
3 T	163.82	167.81	177.36
5 T	270.92	277.51	294.05

From magnetization isotherms we calculated the total magnetic entropy change $|\Delta S_M|$ as a function of temperature and magnetic applied field for all our synthesized samples. According to the thermodynamic theory based on Maxwell relations, $|\Delta S_M|$ can be evaluated through the formula:

$$\Delta S_M(T,H) = S_M(T,H) - S_M(T,0) = \int_0^{H_{\max}} \left(\frac{\partial M}{\partial T}\right)_H dH$$

where $H_{\max}$ is the maximum value of the external magnetic applied field. In practice, for magnetization measurement, this relation can be approximated as:

$$|\Delta S_M| = \sum_i \frac{M_i - M_{i+1}}{T_{i+1} - T_i} \Delta H_i$$

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 [22]. Fig. 4 shows $|\Delta S_M|$ evolution as a function of temperature of $Pr_{0.5}M_{0.1}Sr_{0.4}MnO_3$ (M = Eu, Gd and Dy) samples for different external magnetic applied field. All our samples exhibit

Table 3
Curie temperature T_C, magnetic field change, maximum entropy change $|\Delta S_M^{Max}|$ and RCP values for the present samples and for materials with comparable T_C's from the literature.

Material	T_C (K)	ΔH (T)	$-\Delta S_M$ (J/kg K)	RCP (J/kg)	Reference
$Pr_{0.5}Eu_{0.1}Sr_{0.4}MnO_3$	270	1	1.37	47.93	Present work
$Pr_{0.5}Gd_{0.1}Sr_{0.4}MnO_3$	258	1	1.23	46.02	Present work
$Pr_{0.5}Dy_{0.1}Sr_{0.4}MnO_3$	248	1	1.18	48.29	Present work
$La_{0.7}Ca_{0.3}MnO_3$	256	1	1.38	41	[26]
$La_{0.67}Ba_{0.33}MnO_{2.92}$	275	1	1.8	90	[27]
$Pr_{0.5}Pb_{0.5}MnO_3$	253	1.35	3.34	31	[28]
$La_{0.62}Bi_{0.05}Ca_{0.33}MnO_3$	248	1	3.5	53	[29]
$La_{0.47}Gd_{0.2}Sr_{0.33}MnO_3$	298.5	2	1.59	–	[30]

large MCE effect around T_C due to the large drop in the magnetization. Upon a magnetic field change of 1 T, the maximum entropy change, $|\Delta S_M^{Max}|$, of $Pr_{0.5}Eu_{0.1}Sr_{0.4}MnO_3$ sample reaches the highest value of 1.37 J/kg K at 255 K (Fig. 4c). This value of $|\Delta S_M^{Max}|$ is found to be higher than that reported recently by Suresh Kumar et al. in $Pr_{0.6}Sr_{0.4}MnO_3$ sample ($|\Delta S_M^{Max}| = 0.5$ J/kg K for $\Delta H = 5$ T at 294 K) [23].

The relative cooling power (RCP) is evaluated as $RCP = -\Delta S_M^{Max}(T, H) \times \delta T_{FWHM}$ where δT_{FWHM} is the full-width at half-maximum of $|\Delta S_M|$ versus temperature [24]. For all samples, the RCP values obtained upon different magnetic applied field change of $\Delta H = 1$, 2, 3 and 5 T are summarized in Table 2. The RCP values are, respectively, 270 J/kg, 277 J/kg and 294 J/kg at 5 T for M = Eu, Gd and Dy. These values are, however, lower than the RCP value reported by Pecharsky et al. [25] in Gd or its compounds but high enough for technical interest.

In Table 3, we list the MCE values of the present compounds in comparison with those reported in the literature having comparable T_C's.

Our results may be interesting enough, compared to materials considered as suitable for applications in magnetic refrigerators, opening a way for investigations of materials useful for magnetic refrigeration.

4. Conclusions

In summary, we have presented a study of $Pr_{0.5}M_{0.1}Sr_{0.4}MnO_3$ (M = Eu, Gd and Dy) powder samples through X-ray and magnetic measurements. The structural study shows that all our synthesized samples crystallize in the orthorhombic structure with *Pbnm* space group. All our samples exhibit a paramagnetic–ferromagnetic transition with decreasing temperature. Large MCE has been obtained in all samples at the Curie temperature and $|\Delta S_M^{Max}|$ reaches the highest value of 1.37 J/kg K for the $Pr_{0.5}Eu_{0.1}Sr_{0.4}MnO_3$ sample upon a magnetic applied field change of 1 T. The obtained relative cooling power values of our samples are comparable with other reported values for materials used for magnetic refrigerants.

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