Structural, magnetic and magnetocaloric properties of $R_{2/3}Ba_{1/3}MnO_3$ (R =La,Pr) manganites

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Structural, magnetic and magnetocaloric properties of $La_{2/3}Ba_{1/3}MnO_3$ and $Pr_{2/3}Ba_{1/3}MnO_3$ manganites with perovskite type structure were studied. The magnetic measurements were performed in the temperature range 4.2 – 700K and external magnetic fields up to 7T. The adiabatic magnetic entropy changes, $|\Delta S_M|$, were determined from magnetization data. Transition temperature is around 360K for R = La and 190K for R=Pr. A large magnetocaloric effect (MCE) has been obtained in studied samples with a considerable value of relative cooling power (RCP).

1. Introduction

MCE was discovered in 1881 by Warburg in iron [1]. Magnetic materials showing a large magnetocaloric effect have attracted considerable attention for their potential application in magnetic refrigeration technology [2, 3].
The interest in developing new materials with magnetocaloric properties has increased considerably after the discovery of giant magnetocaloric effect (GMCE) in alloys $Gd_5Si_2Ge_2$[2]. A class of materials with suitable properties for magnetic refrigeration (MR) at room temperature are the manganites with perovskite type structure [3, 4] which present a large magnetocaloric effect. These materials are easily obtained and have a low production cost. In present time, there is a growing interest regarding the use of magnetic refrigeration in technical applications [5]. There are some important advantages in using this technique: no compressor (with high production cost and mechanical vibrations), this cooling techniqueis an eco-friendly method (it gives up to the solvents used in conventional refrigerators) and the high mechanical efficiency of this technique [6]. Magnetic refrigeration is based on magnetocaloric effect (MCE). MCE in magnetic materials is high at low temperatures close to the temperature of liquid nitrogen or liquid helium.In recent years some studies have been developed to use this technique of refrigeration in the fields of temperatures around room temperature [7, 8]. This effect consists in cooling or heating of a magnetic material when a magnetic field is applied. The total entropy of any material is described by sum of electrons entropy (S_{el}), the crystal lattice entropy (S_{lat}) and the magnetic entropy (S_M)

$$S_{tot} = S_{el} + S_{lat} + S_M \qquad (1)$$

MCE can be quantify by the value of the magnetic entropy change ΔS_M. We want to obtain large values of magnetic entropy change ΔS_M for small values of the applied magnetic field. Magnetic field values up to 3T can be obtained by using some types of permanent magnets [9]. These magnets could then be used in the magnetic refrigeration technique [6]. Magnetic entropy change can be determined from magnetisation isotherms at different temperatures using the Maxwell equation

$$\Delta S_M = \int_0^H \left(\frac{\partial M}{\partial T}\right)_H dH \qquad (2)$$

Another important factor in the choice of materials used as good refrigerant in magnetic refrigeration technique is relative cooling power (RCP)

$$RCP = |\Delta S_M|_{max} \times \delta T_{FWHM} \qquad (3)$$

where $|\Delta S_M|_{max}$ is the maximum of the magnetic entropy change and δT_{FWHM} is the full-width at half-maximum in the temperature dependence of the magnetic entropy change ΔS_M.
In present work, we have studied comparatively the crystal structure of $R_{2/3}Ba_{1/3}MnO_3$ (R = La and Pr), the magnetic properties and the magnetocaloric effect.

2. Experimental

Polycrystalline samples with compositions $La_{2/3}Ba_{1/3}MnO_3$ (LBMO) and $Pr_{2/3}Ba_{1/3}MnO_3$ (PBMO) were prepared by a conventional ceramic sintering method using 99.9% high purity materials from Sigma-Aldrich: La_2O_3, Pr_2O_3, $BaCO_3$, MnO_2. In order to obtain the samples (keeping good stochiometry of systems) the powders of constituent elements were mixed. The samples in the form of powders were calcined at 1000°C for 24 hours and then sintered at 1300°C in air for 24 hours using

a Nobertherm heat treatment furnace. The procedure of calcination was repeated several times. The X-ray diffraction patterns were analyzed by using a Bruker D8 Discover diffractometer with CuKα radiation ($λ=1.54056$Å) from 20-60° with a step of 0.2°. The vibrating sample magnetometer (VSM) of a 7 Tesla Mini Cryogenfree Measurement System (CryogenicLtd.) was used for magnetization measurements in the temperature range 5–500K and in magnetic fields up to 5T [10]. The temperature dependence of magnetization, $M(T)$, was recorded on warming under 0.1T applied magnetic field. The sample was cooled to 5K in zero field and data were taken while warming after establishing the magnetic field. To estimate the magnetocaloric effect, the isothermal magnetization measurements were performed at selected temperatures, ramping up the magnetic field (continuously) from 0 to 5T. The magnetocaloric effect was calculated for magnetic field variations $μ_0H=0–5T$. The magnetocaloric effect can be determined by calculating the magnetic entropy change between zero field (minimum) and $μ_0H=5T$ (maximum field).

3. Results and discussion

The X-ray diffraction patters showed that the compounds present one single phase. The compounds crystallize in a rhombohedral type structure (GS:$R\bar{3}c$, Z=6). The crystal structure was further refined by the FullProf Suit software for Rietveld analysis [11]. Fig.1. and Fig.2. shown the X-ray diffraction patterns and fitted results. Vertical lines represent position of Bragg reflections and continue blue line represent the difference between observed and calculated values.
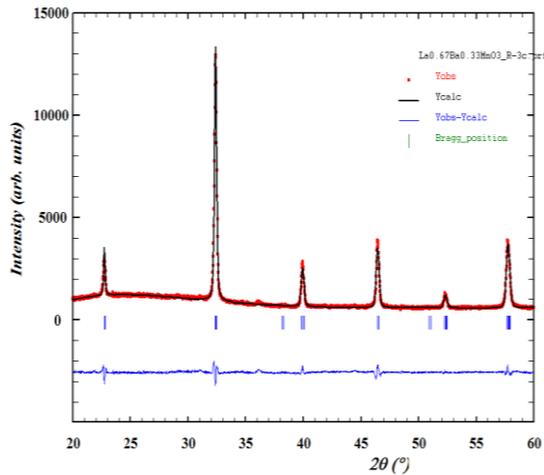
Fig.1. X-ray diffraction diagram of $La_{2/3}Ba_{1/3}MnO_3$ fitted with Rietveld method

The fitting results show that the lattice parameters of the samples decrease slightly when Lanthanum (La) is substituted by Praseodymium (Pr). For LBMO the lattice parameters are: a=5.523 Å and c = 13.562 Å respectively, and a= 5.506 Å and c = 13.489 Å for PBMO.

This decrease is due to the fact that the ionic radius of the Pr atom r_{Pr}^{3+}= 1.013 Å is smaller than the ionic radius of La atom r_{La}^{3+}= 1.061 Å.
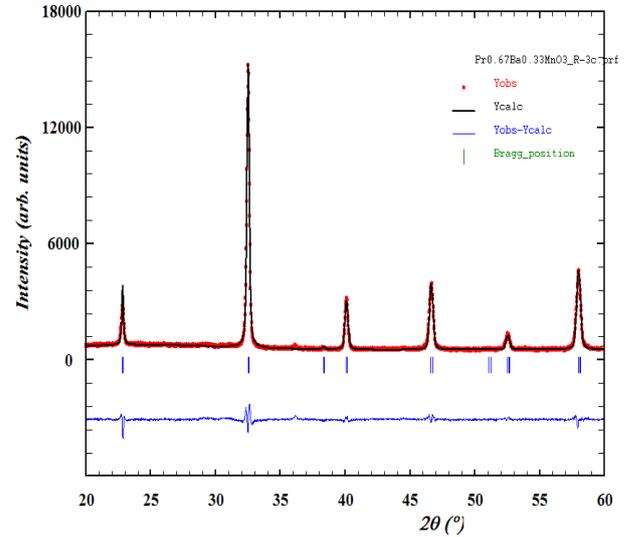
Fig.2. X-ray diffraction diagram of $Pr_{2/3}Ba_{1/3}MnO_3$ fitted with Rietveld method
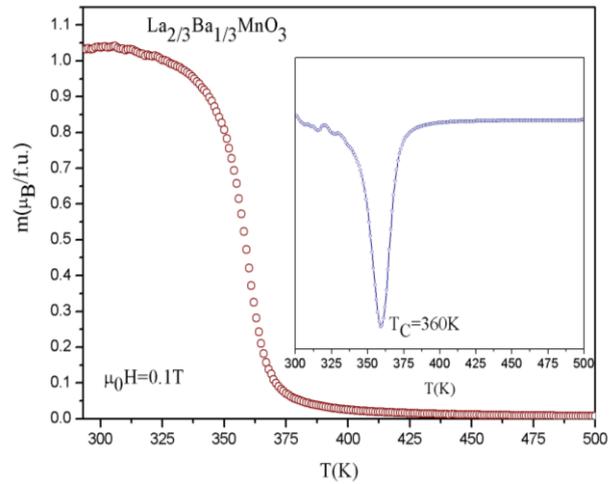
Fig.3. Temperature dependence of magnetization of $La_{2/3}Ba_{1/3}MnO_3$ taken in 0.1T persistent magnetic field.In the inset: dM(T)/dT.

To determine the transition temperature the thermomagnetic analysis was performed. The magnetization for the compound with R=La was measured in the temperature range from 275K to 500 K in an applied magnetic field of 0.1T and increased temperature up to 500K (Fig.3.). The transition temperature was found from the first order derivative of magnetization versus temperature.

It is shown in the inset of Fig.3. The compound with R=Pr was measured in the temperature range from 100K to 250 K (Fig.4.).

The Curie temperatures T_c obtained for the two compounds are: for the compound with R = La, $T_c = 360K$ and for the compound with R = Pr, $T_c = 197K$.

The magnetization isotherms were measured ramping the applied magnetic field from zero to 5 T in a temperature range of about ±50 K around the transition temperature T_c.
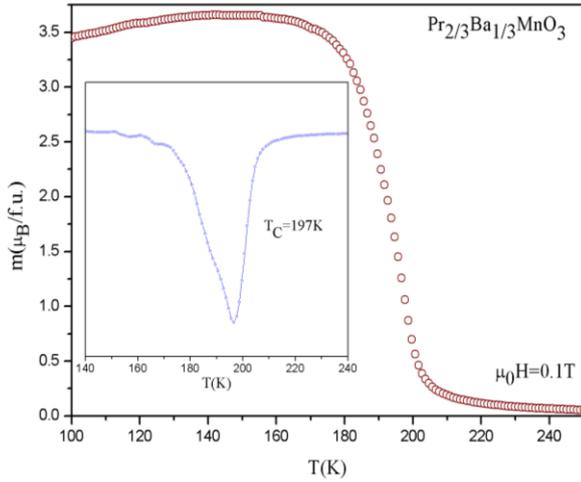
Fig.4. Temperature dependence of magnetization of $Pr_{2/3}Ba_{1/3}MnO_3$ taken in 0.1T persistent magnetic field. In the inset :dM(T)/dT.

Between two consecutive magnetization isotherm the increment of temperature was of 5K ($\Delta T = 5K$) [12]. The increase of the applied magnetic field, μ_0H, was in steps of 0.1 T. The magnetization isotherms for the compound with R = La is shown in Fig.5. and for compound with R = Pr can be seen in Fig.6.
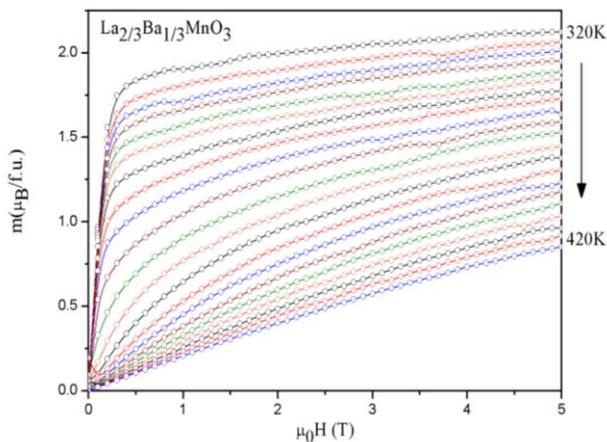
Fig.5. Magnetization isotherms for the compound $La_{2/3}Ba_{1/3}MnO_3$

The magnetization isotherms for the compound with R=La was measured in the temperature range from 320K to 420K and the magnetization isotherms for the compound with R=Pr was measured in the temperature range from 150K to 260K. In case of the compound with

R = La the first magnetization isotherm was made at T = 320K (before T_c) and the last magnetization isotherm was made at T=420K (above T_c). We can see that the first isotherms show a ferromagnetic (FM) behaviour and the shape of last isotherm is typical for a paramagnetic (PM) material. The same behaviour can be observed in case of the compound with R=Pr. First magnetization isotherm was made at T=150K (before T_c) and the last magnetization isotherm was made at T=260K (above T_c).
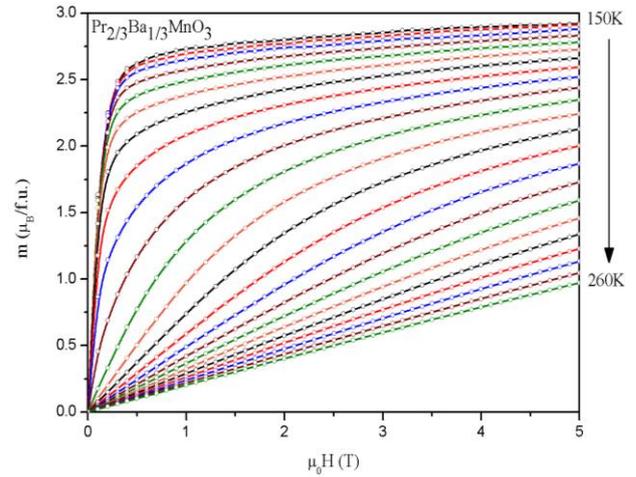
Fig.6. Magnetization isotherms for the compound $Pr_{2/3}Ba_{1/3}MnO_3$

To study the nature of magnetic transition we have built the Arrott plots [13] for the two compounds.
Using the Banerjee criterion [14] we can determine if we have a first order transition or a second order transition using magnetic methods.
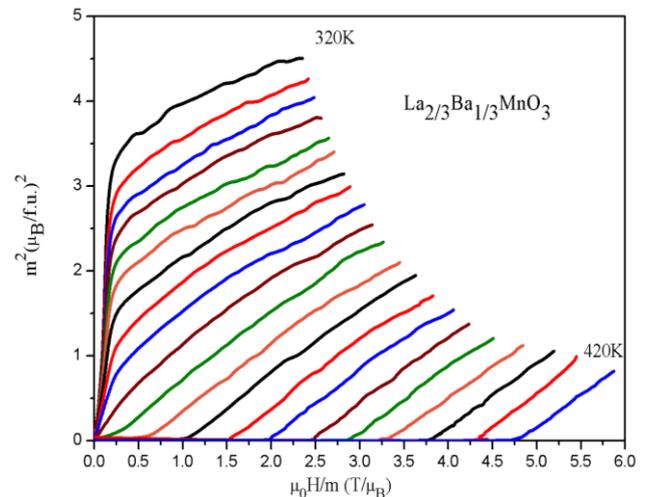
Fig.7. Arrott plots for the compound $La_{2/3}Ba_{1/3}MnO_3$

According to this criterion if the slopes of the curves of m^2 vs. (μ_0H/m) near T_c are positive then the material present a second order transition. If the magnetic isotherms have a negative slope then the transition is first order.
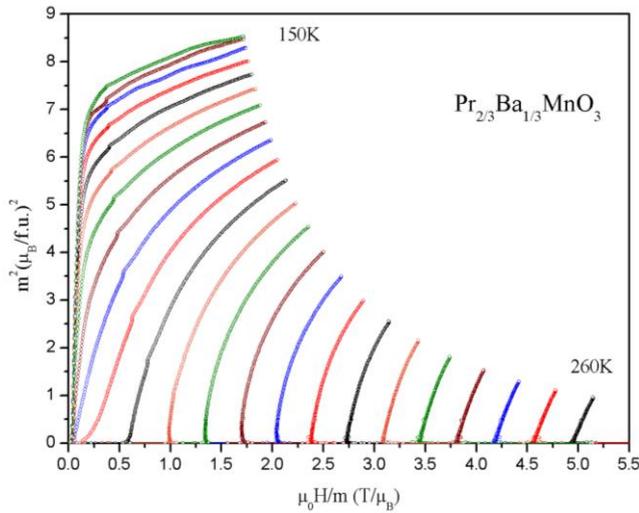
Fig.8. Arrott plots for the compound $Pr_{2/3}Ba_{1/3}MnO_3$

In according with the mean-field theory those magnetic isotherms should be straight lines around critical region (transition) and pass through the origin. It's easy to see from the diagram that curves are not linear, especially in the small fields. The linearity of Arrott curves is better in the high magnetic field region. The slopes of these curves were positive, indicating that the transition is second order transition for both investigated samples (Fig.7. Fig.8.). The negative slopes or inflection points in the Arrott plots often indicate a first-order phase transition. This criterion has been used in disorder-order transitions between PM and FM states [15, 16].
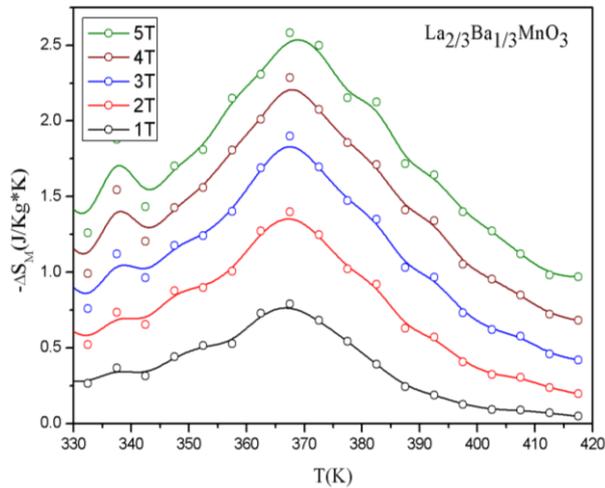
Fig.9. The magnetic entropy change for the compound $La_{2/3}Ba_{1/3}MnO_3$

From the magnetization isotherms we calculated the magnetic entropy change $\Delta S_M(T,H)$ using the approximation

$$\Delta S_M(T, H_0) = S_M(T, H_0) - S_M(T, 0) =$$

$$= \frac{1}{\Delta T} \int_0^{H_0} [M(T + \Delta T, H) - M(T, H)]\, dH \quad (4)$$

where ΔT represent the temperature increment between two consecutive isotherms [10, 12]. The temperature dependence of the magnetic entropy change $-\Delta S_M$(J/KgK) when $\mu_0\Delta H$= 1, 2,..., 5 T are plotted in Fig.9 and Fig.10 for $La_{2/3}Ba_{1/3}MnO_3$ and $Pr_{2/3}Ba_{1/3}MnO_3$.respectively.
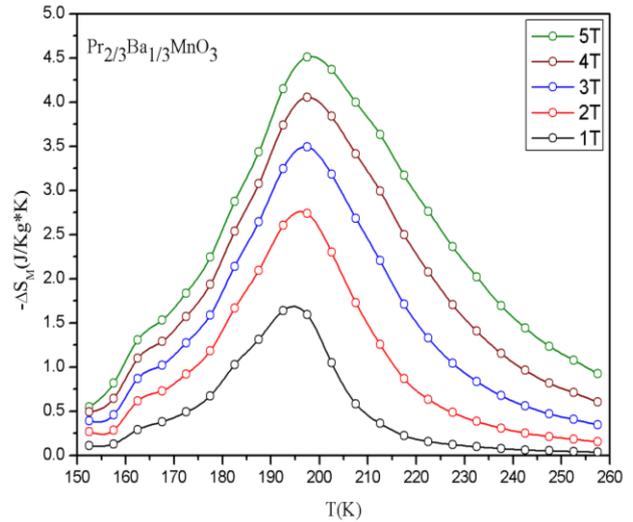
Fig.10. The magnetic entropy change for the compound $Pr_{2/3}Ba_{1/3}MnO_3$

For the maximum value of the magnetic field change $\mu_0\Delta H$=5 T, the value of $|\Delta S_M|_{max}$ was 2.58J/KgK for the R = La compound ($La_{2/3}Ba_{1/3}MnO_3$), while for R = Pr compound ($Pr_{2/3}Ba_{1/3}MnO_3$) we have found 4.51J/KgK for $|\Delta S_M|_{max}$. The results of these measurements are summarized in Table 1

Table 1. Maximum entropy changes ΔS_{max} for $La_{2/3}Ba_{1/3}MnO_3$ and $Pr_{2/3}Ba_{1/3}MnO_3$

$\mu_0\Delta H$ (T)	$|\Delta S_M|$(J/KgK)	
	$La_{2/3}Ba_{1/3}MnO_3$	$Pr_{2/3}Ba_{1/3}MnO_3$
1	0.79	1.59
2	1.39	2.73
3	1.89	3.49
4	2.28	4.05
5	2.58	4.51

In Fig. 11. we represented the maximum values of the magnetic entropy change $|\Delta S_M|_{max}$ at T_C for each of the samples for magnetic field changes $\mu_0\Delta H$=0;1;2;3;4 and 5T.
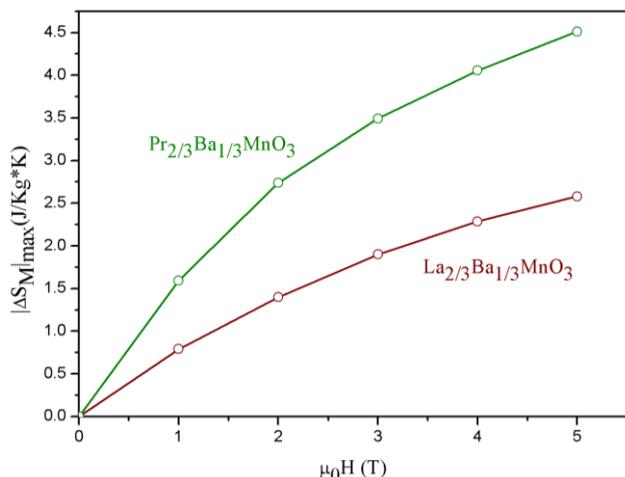
Fig.11. Field dependence of maximum values of the magnetic entropy change $|\Delta S_M|_{max}$ for each sample at T_C.

The RCP values were plotted in Fig.12. We can observe a good linearity of the data which is important for a magnetic refrigerator.

As can be seen from Fig.12 the compound $Pr_{2/3}Ba_{1/3}MnO_3$ has very large RCP values, which recommend it as a magnetocaloric material that could be used in technical applications. $La_{2/3}Ba_{1/3}MnO_3$ has a moderate magnetocaloric effect at temperatures situated above the room temperature.

As a next step we will search to lower this temperature (with some appropriate ion substitutions), while keeping the magnitude of the magnetocaloric effect.
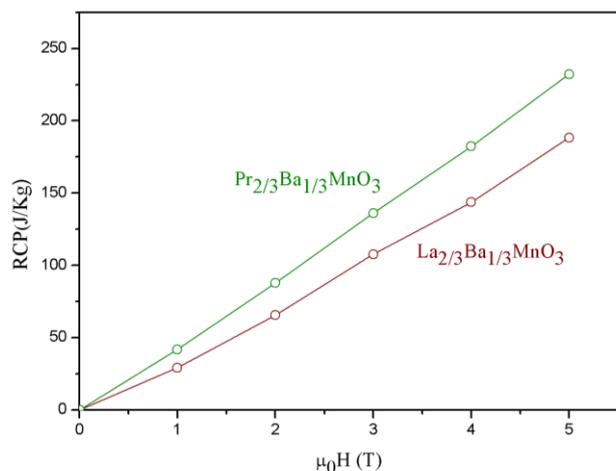
Fig.12. Relative cooling power RCP as a function of magnetic field.

In Table 2, the values of relative cooling power (RCP) for both compounds are given.

Table 2. Relative cooling powers (RCP) calculated for $La_{2/3}Ba_{1/3}MnO_3$ and $Pr_{2/3}Ba_{1/3}MnO_3$

$\mu_0 \Delta H$ (T)	RCP (J/Kg)	
	$La_{2/3}Ba_{1/3}MnO_3$	$Pr_{2/3}Ba_{1/3}MnO_3$
1	29	41
2	65	87
3	107	136
4	143	182
5	188	232

4. Conclusions

Polycrystalline samples $La_{2/3}Ba_{1/3}MnO_3$ and $Pr_{2/3}Ba_{1/3}MnO_3$ were investigated for their magnetic and magnetocaloric properties. All the samples present one single phase with rhombohedral $R\bar{3}c$ type structure.

The compounds show second-order transitions from PM to FM phase. The Curie temperatures were 360 K for $La_{2/3}Ba_{1/3}MnO_3$ and 197 K for $Pr_{2/3}Ba_{1/3}MnO_3$. The maximum value of magnetic entropy change is $|\Delta S_M|_{max}$=2.58J/kg·K at $\mu_0\Delta H$=5 T for R = La and $|\Delta S_M|_{max}$=4.51J/kg·K at $\mu_0\Delta H$=5 T for R = Pr. The RCP have large values comparable with the values obtained in other perovskite-type compounds [17], which is of interest for magnetic refrigeration (RCP=188 J/Kg for R = La and RCP = 232 J/Kg for R = Pr).

The studied compounds may be considered as potential magnetocaloric materials operated in the 200-350K temperature range.

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