Magnetic and Magnetocaloric Properties of Monovalent Substituted \( \text{La}_{0.65}\text{M}_{0.3}\text{M'}_{0.05}\text{MnO}_3 \) (\( \text{M}=\text{Ba}, \text{Ca} \) and \( \text{M'}=\text{Na}, \text{Ag}, \text{K} \)) Perovskite Manganites

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Abstract

The effects of monovalent doping in the A-site on the structural, magnetic and magnetocaloric properties in \( \text{La}_{0.65}\text{M}_{0.3}\text{M'}_{0.05}\text{MnO}_3 \) (\( \text{M}=\text{Ba}, \text{Ca} \) and \( \text{M'}=\text{Na}, \text{Ag}, \text{K} \)) powder perovskite manganites have been investigated. Our samples have been synthesized by the conventional solid state reaction at high temperature. X-ray diffraction analysis using the Rietveld refinement show that all our synthesized samples are single phase and crystallize in the orthorhombic structure with \( \text{Pbnm} \) space group for the samples where the A-site is occupied by Ca and monovalent element and in the rhombohedral system with \( \text{R3c} \) space group for the samples where the A-site is occupied by Ba and monovalent element. Magnetization measurements versus temperature in a magnetic applied field of 50 mT indicate that all our investigated samples display a paramagnetic-ferromagnetic transition with decreasing temperature. A positive slope in the isotherm plots of \( \text{M}^2 \) versus \( \text{H}/\text{M} \) is a clear indication of a second order phase transition from ferromagnetic to paramagnetic phase. From the measured magnetization data of \( \text{La}_{0.65}\text{M}_{0.3}\text{M'}_{0.05}\text{MnO}_3 \) (\( \text{M}=\text{Ca}, \text{Ba} \) and \( \text{M'}=\text{Na}, \text{Ag}, \text{K} \)) samples as a function of magnetic applied field, the associated magnetic entropy change, \( \Delta S_m \), close to their respective Curie temperature and the relative cooling power RCP have been determined. The \( \text{La}_{0.65}\text{Ca}_{0.3}\text{Ag}_{0.05}\text{MnO}_3 \) compound has the highest \( \Delta S_m \) value of 5.16 J/KgK at 245 K upon a magnetic field change of 5 T. The RCP values are comparable and almost the same for both series (about 70% of that of pure Gd), indicating that our compounds are suitable candidates to be used in magnetic refrigeration

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1. Introduction

Recently, magnetic refrigeration based on magnetocaloric effect (MCE) has attracted considerable attention as it offers more considerable advantages than the conventional thermomechanical cooling techniques [1-3]. The MCE is

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an intrinsic property of a magnetic material arising due to the coupling of magnetic sub-lattice with the magnetic field. Increasing the strength of the applied magnetic field in a ferromagnetic material induces the alignment of the magnetic moments with the direction of the magnetic field which leads to a decrease of the spin entropy. This process is accompanied by a rise of the lattice entropy when the field is applied adiabatically. However, if we remove the magnetic applied field, the spin system tends to randomize which increases the spin entropy, reduces the lattice one and consequently lowers the temperature of the system. The search of a room temperature magnetic refrigerant is of special interest. The most studied compounds in this area are Gd$_5$(Si$_{1-x}$Ge$_x$)$_4$ [4], Mn$_{3}$As$_{1-x}$Sb$_x$ [5], MnFeP(O$_{0.45}$As$_{0.55}$) [6], La(Fe$_{1-x}$Si$_{x}$)$_{12}$ [7] and the perovskite manganites [8]. Manganites are interesting in application as potential candidates in magnetic refrigeration since they are cheap, easy to fabricate, possess tunable T$_c$ and high chemical stability.

According to the classical thermo-dynamical theory, the magnetic entropy change, $\Delta S_m$, produced by the variation of a magnetic field from 0 to $H_0$ is given by:

$$\Delta S_m(T,H_0) = S_m(T,H_0) - S_m(T,0) = \int_0^{H_0} \frac{\partial S}{\partial H} \, dH$$

(1)

with Maxwell’s relation:

$$\left(\frac{\partial S}{\partial H}\right)_T = \left(\frac{\partial M}{\partial T}\right)_H$$

(2)

one obtains the following expression [9]:

$$\Delta S_m(T,H_0) = \int_0^{H_0} \frac{\partial M}{\partial T} \left|_{T_0} \right. \, dH$$

(3)

For magnetization measured at discrete field and temperature intervals, the magnetic entropy change defined in Eq. (3) can be approximated by:

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

(4)

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 $H_i$ [10]. Using Eq. (4), by measuring the M–H curve at several temperatures, one can calculate the magnetic entropy change associated with the magnetic field variation. In the present work, we elaborated by the solid state method at high temperature the La$_{0.65}$(Ca, Ba)$_{0.3}$M$_{0.05}$MnO$_3$ powder samples and investigated the effect of the monovalent doping on their structural, magnetic and magnetocaloric properties.

2. Experimental techniques

Polycrystalline samples of La$_{0.65}$M$_{0.3}$M'$_{0.05}$MnO$_3$ (M= Ba, Ca and M'=Na, Ag, K) were synthesized using the 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 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. Structural analysis was carried out using the standard Rietveld method [11-12]. Magnetization measurements versus temperature in the range 20–350 K and versus magnetic applied field up to 7 T were carried out using a vibrating
sample magnetometer. MCE were deduced from the magnetization measurements versus magnetic applied field up to 7 T at several temperatures.

3. Results and discussion

In both series \(La_{0.65}Ca_{0.3}M_{0.05}MnO_3\) and \(La_{0.65}Ba_{0.3}M_{0.05}MnO_3\) (\(M=Na, Ag, K\)), the \(Mn^{4+}\) amount remains constant equal to 40%. Monovalent element doping leads to a change in the average ionic radius <r_A> and in the mismatch size \(\sigma^2\) of the A-cation site. The X-ray diffraction (XRD) patterns of all our synthesized powder samples were recorded at room temperature and based on these patterns, their crystal structures were refined by Rietveld’s profile-fitting method. The profile refinement is started with scale and background parameters followed by the unit cell parameters. Then, the peak asymmetry and preferred orientation corrections are applied. Finally, the positional parameters and the individual isotropic parameters are refined. Samples with \(M=Ca\) crystallize in the orthorhombic phase with Pbnm space group, while samples with \(M=Ba\) crystallize in the rhombohedral system with \(R\bar{3}m\) space group. Typical experimental and refined XRD patterns for two representative samples \(La_{0.65}Ca_{0.3}Na_{0.05}MnO_3\) and \(La_{0.65}Ba_{0.3}Na_{0.05}MnO_3\) are shown in Fig. 1.

For both series, the unit cell volume increases slightly with increasing the ionic radius of the A-site (Fig. 2). For \(La_{0.65}Ca_{0.3}M'_{0.05}MnO_3\) samples, the orthorhombicity defined as \(O\%=(b-a)/(b+a)\times100\) decreases from 0.31% for \(M=Na\) to 0.13% for \(M=K\). This indicated that the structure tends towards pseudo-cubic symmetry as <r_A> increases.

![Fig. 1: XRD patterns of \(La_{0.65}M'_{0.3}Na_{0.05}MnO_3\) compounds. (a) \(M=Ca\) and (b) \(M=Ba\).](image)

![Fig. 2: Unit cell evolution versus <r_A> for \(La_{0.65}M'_{0.3}MnO_3\) compounds: (a) \(M=Ca\) and (b) \(M=Ba\).](image)
For La\textsubscript{0.65}Ba\textsubscript{0.3}M’\textsubscript{0.05}MnO\textsubscript{3} samples, the values of the MnO\textsubscript{6} octahedral tilts around the [111] direction, determined from the oxygen positions, are 5.1°, 8.5°, and 8.7° for M’=Na, Ag and K respectively. As a result, the strength of the double exchange interaction between adjacent Mn\textsuperscript{3+} and Mn\textsuperscript{4+} ions decreases with increasing both <r\textsubscript{A}> and \sigma\textsuperscript{2} leading to a weakening of the Curie temperature as will be discussed below.

Magnetization measurements as a function of temperature in the range 20-300K and in a magnetic applied field of 50mT showed that all our synthesized samples exhibit a paramagnetic to ferromagnetic transition with decreasing temperature (Fig. 3).

![Magnetization as a function of temperature for La\textsubscript{0.65}M\textsubscript{0.3}M’\textsubscript{0.05}MnO\textsubscript{3} samples at \mu_0H=50mT (M=Ca,Ba and M’=Na,Ag,K).](image)

The T\textsubscript{C} values of the two series of samples, determined from the inflexion point of the magnetization curves, can be governed via at least two factors: <r\textsubscript{A}> and \sigma\textsuperscript{2}, which may interact. It has been reported by various authors that in manganites, large values of \sigma\textsuperscript{2} induce a lowering of the bandwidth of the \epsilon\textsubscript{g} electrons and consequently leading to a T\textsubscript{C} decrease [13]. For both series, as can be seen from Fig. 4, the highest value of T\textsubscript{C} is observed for M=Na which correspond to the lowers values of both <r\textsubscript{A}> and \sigma\textsuperscript{2}.

![Curie temperature T\textsubscript{C} and \sigma\textsuperscript{2} evolution versus <r\textsubscript{A}> for (a) La\textsubscript{0.65}Ca\textsubscript{0.3}M’\textsubscript{0.05}MnO\textsubscript{3} and (b) La\textsubscript{0.65}Ba\textsubscript{0.3}M’\textsubscript{0.05}MnO\textsubscript{3} samples (M’=Na,Ag,K).](image)
For La$_{0.65}$Ca$_{0.3}$M'+0.05MnO$_3$ samples (Fig. 4a), $T_C$ firstly decreases with $\langle R_A \rangle$ and $\sigma^2$, and then increases with further increasing $\langle R_A \rangle$ (M'=K), indicating that the $\langle R_A \rangle$ prevails over mismatch effect for M'=K sample. The $T_C$ decrease with increasing $\sigma^2$ in La$_{0.65}$Ba$_{0.3}$M'+0.05MnO$_3$ samples (Fig. 4b) may be understood in terms of increasing $\sigma^2$ which leads to the presence of microscopic phase formation at the grain boundaries [14]. In order to confirm the ferromagnetic behavior of our samples at low temperatures, we performed magnetization measurements versus magnetic applied field up to 8T at several temperatures. It is shown in Fig. 5 for the two samples La$_{0.65}$Ca$_{0.3}$K$_{0.05}$MnO$_3$ and La$_{0.65}$Ba$_{0.3}$K$_{0.05}$MnO$_3$.

Fig. 5. Magnetization evolution versus magnetic applied field at several temperatures for (a) La$_{0.65}$Ca$_{0.3}$K$_{0.05}$MnO$_3$ and (b) La$_{0.65}$Ba$_{0.3}$K$_{0.05}$MnO$_3$ samples.

Below $T_C$, the magnetization $M$ increases sharply with magnetic applied field up to 1T and then saturates. The experimental value of the spontaneous magnetization $M_{sp}(exp)$, deduced from the M(H) curves is found to be 3.23μB/Mn and 3.10μB/Mn for La$_{0.65}$Ca$_{0.3}$K$_{0.05}$MnO$_3$ and La$_{0.65}$Ba$_{0.3}$K$_{0.05}$MnO$_3$ respectively. The magnitude of the $M_{sp}(exp)$ is smaller than the theoretical value of 3.6μB/Mn calculated for full spin alignment.

Fig. 6a-b show the Arrott plots (M$^2$ versus H/M) obtained from magnetization isotherms. As can be seen, Arrott plots show a positive slope which indicates that a second order magnetic transition occurs in our samples [15].

Fig. 6. M$^2$ versus H/M isotherms for (a) La$_{0.65}$Ca$_{0.3}$K$_{0.05}$MnO$_3$ and (b) La$_{0.65}$Ba$_{0.3}$K$_{0.05}$MnO$_3$ samples.
The isothermal magnetic entropy change, $\Delta S_m$, has been calculated from the magnetization isotherms for all our synthesized samples, and it is shown in Fig. 7 for a 0-5T magnetic applied field change.

As expected, for all samples, $\Delta S_m$ has its maximum in the vicinity of the Curie temperature $T_C$, where the magnetization undergoes a sudden variation at this temperature. The sign of $\Delta S_m$ is negative, which means that heat is liberated when the magnetic field is changed adiabatically. The La$_{0.65}$Ca$_{0.3}$Ag$_{0.05}$MnO$_3$ compound has the highest $\Delta S_m$ value of 5.16J/kgK at 245K upon a magnetic field change of 5 T. The substitution of Ca by monovalent element increases the $T_C$ value, but drives the maximum of magnetic entropy change, $\Delta S_{m,\text{Max}}$, to lower values. It can be seen that, for the same magnetic applied field change of 5 T, with increasing $<r_{A}>$ from 1.149Å (M=Na) to 1.165 Å (M=K), $\Delta S_{m,\text{Max}}$ increases from 3J/kgK to 3.54J/kgK while $T_C$ decreases. This behavior is in contrast with the behavior of La$_{0.7}$Ca$_{0.3-x}$Ba$_x$MnO$_3$ compounds, whose Curie temperature increases with $<r_{A}>$, and whose $\Delta S_{m,\text{Max}}$ shows a slight decrease with $<r_{A}>$ [16]. For La$_{0.65}$Ba$_{0.3}$M$'_{0.05}$MnO$_3$ samples, $\Delta S_m$ remains almost constant despite the dependence of $T_C$ on $<r_{A}>$. This later result concerning the magnetic entropy change seems to be related to the constant value of the Mn$^{4+}$/Mn$^{3+}$ ratio. It is interesting to note that the origin of the large magnetic entropy change should be attributed also to the coupling between spin and lattice in the magnetic ordering process [17], which seems to be the same in our samples. For a composite magnetic refrigerant composed by La$_{0.65}$Ba$_{0.3}$Na$_{0.05}$MnO$_3$, La$_{0.65}$Ba$_{0.3}$Ag$_{0.05}$MnO$_3$ and La$_{0.65}$Ba$_{0.3}$K$_{0.05}$MnO$_3$ samples with slightly different transition temperatures, the $\Delta S_m$ of the system is more broadened in a wide range of temperatures around room temperature, which is important for active magnetic refrigeration (AMR) [18]. In the magnetic refrigeration technology, it is of utmost interest that the magnetocaloric effect extends over a large temperature range; we can than consider the magnitude of $\Delta S_{m,\text{Max}}$ and its full-width at half-maximum, known as the relative cooling power (RCP) [19] given by:

$$\text{RCP} = -\Delta S_m(T,H) \times \delta T_{\text{max}}$$

We have plotted in Fig. 8 the RCP values as a function of $T_C$ for both series upon a magnetic field change of 5T in comparison with Gd metal which is considered as the most active refrigerant near room temperature. We can
notice that although \(\Delta S_m\) values are different mainly for \(La_{0.65}Ca_{0.3}M_{0.05}MnO_3\) samples, the RCP values are comparable and almost the same for both series (about 70\% of that of pure Gd), indicating that our compounds are suitable candidates to be used in magnetic refrigeration.

![Fig. 8. RCP values versus TC for \(La_{0.65}Ca_{0.3}MnO_3\), \(La_{0.65}Ba_{0.3}MnO_3\), and Gd](image)

4. Conclusion

In conclusion, \(La_{0.65}Ca_{0.3}M'_{0.05}MnO_3\) and \(La_{0.65}Ba_{0.3}M'_{0.05}MnO_3\) (\(M'\)=Na, Ag, K) samples have been synthesized by the solid state reaction method at high temperature. The substitution of Ca or Ba by a small amount of monovalent element changes the lattice parameters and affects the exchange interaction, which influences the magnetic and magnetocaloric properties. All our samples exhibit a paramagnetic-ferromagnetic transition with decreasing temperature. These compounds exhibit a maximum of magnetic entropy change \(\Delta S_m\) in the vicinity of the Curie temperature \(T_C\). Varying the A-site ionic radii in \(La_{0.65}Ca_{0.3}M'_{0.05}MnO_3\) compounds offers the possibility of tuning the \(T_C\) to the room temperature region. Large \(\Delta S_m\) value of 5.16J/KgK at 245K upon a magnetic field change of 5T has been achieved for \(La_{0.65}Ca_{0.3}Ag_{0.05}MnO_3\). Large relative cooling power (RCP) value of 290J/kg is obtained for \(La_{0.65}Ba_{0.3}Na_{0.05}MnO_3\) sample, at a field change of 5T. This relatively large value associated to a Curie temperature of 310K make the present compound a promising candidate for magnetic refrigerators around room temperature.

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