Magnetic and magnetocaloric properties of monovalent substituted $\text{La}_{0.65}\text{Ca}_{0.3}\text{M}_{0.05}\text{MnO}_3$ ($\text{M}=\text{Na}, \text{Ag}, \text{K}$) perovskite manganites

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Abstract. The effects of monovalent doping in the A-site on the structural, magnetic and magnetocaloric properties in $\text{La}_{0.65}\text{Ca}_{0.3}\text{M}_{0.05}\text{MnO}_3$ ($\text{M}=\text{Na}, \text{Ag}, \text{K}$) powder perovskite manganites have been investigated. Our samples have been synthesized using the conventional solid state reaction at high temperature. Rietveld refinements of the X-ray diffraction patterns at room temperature show that all our powder samples are single phase and crystallize in the orthorhombic structure with Pbnm space group. Magnetization measurements versus temperature in a magnetic applied field of 50mT indicate that our investigated samples display a paramagnetic-ferromagnetic transition with decreasing temperature. The Curie temperature $T_C$ is found to be 295K, 254K and 285K for $\text{M}=\text{Na}$, Ag and K respectively. From the measured magnetization data of $\text{La}_{0.65}\text{Ca}_{0.3}\text{M}_{0.05}\text{MnO}_3$ ($\text{M}=\text{Na}, \text{Ag}, \text{K}$) samples as a function of magnetic applied field, the associated magnetic entropy change close to their respective Curie temperature $T_C$ and the relative cooling power RCP have been determined. The maximum magnetic entropy change, $\Delta S_m^{\text{max}}$, in a magnetic field change of 5T is found to be 3, 5.16 and 3.54 Jkg/K for $\text{M}=\text{Na}$, Ag and K respectively. The $\text{La}_{0.65}\text{Ca}_{0.3}\text{K}_{0.05}\text{MnO}_3$ sample exhibits the largest RCP value of 295J/kg.

1. Introduction

The magnetoresistive oxides $\text{RE}_{1-x}\text{M}_x\text{MnO}_3$ ($\text{RE}=\text{La}, \text{Pr}, ...$ and $\text{M}=\text{Ca}, \text{Sr}, \text{Ba}, ...$) provide a rich variety of structural, magnetic and transport properties depending on the doping concentration ($\text{Mn}^{3+}/\text{Mn}^{4+}$ ratio), the average size of A cation-site $<r_A>$ which controls the effective electron bandwidth $W$ and the mismatch effect [1,2]. Recently, novel properties have been observed in perovskite-type ferromagnetic manganese oxides related to magnetocaloric effect (MCE) [3,4]. The MCE originates from the heating or the cooling of magnetic material due to the application of 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. Pecharsky and Gschneidner [5-6] discovered a giant MCE in the pseudo-binary alloy Gd$_5$(Si$_x$Ge$_{1-x}$)$_4$ in the temperature range 50-280K. More recently, giant MCE at about 300K has been measured in MnFeP(O$_{0.45}$As$_{0.55}$) [7]. An overview of the magnetocaloric properties in perovskite manganese oxides have been provided by Phan and Yu [8]. In the present work, we synthesized La$_{0.65}$Ca$_{0.30}$M$_{0.05}$MnO$_3$ (M=Na, Ag and K) powder perovskite manganites by the conventional solid state reaction at high temperature and studied the crystallographic, magnetic and magnetocaloric effects due to the substitution of 5% of calcium by monoivalent element Na, K and Ag.

2. Experimental techniques
Polycrystalline samples of La$_{0.65}$Ca$_{0.30}$M$_{0.05}$MnO$_3$ (M=Na, K and Ag) were synthesized using the solid state reaction method at high temperature by mixing La$_2$O$_3$, CaCO$_3$, MnO$_2$ and A$_2$CO$_3$ (A=Na, Ag and K) up to 99.9% high purity in the desired proportion. The starting materials were intimately mixed in an agate mortar and then heated in air up to 1000°C for 60h. The obtained powders were then pressed into pellets (of about 1mm thickness) and sintered at 1100°C in air for 60h 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 Rielveld method [9]. Magnetization measurements versus temperature in the range 20–350K and versus magnetic applied field up to 7T were carried out using a vibrating sample magnetometer. MCE were deduced from the magnetization measurements versus magnetic applied field up to 7T at several temperatures.

3. Results and discussions
X-Ray powder diffraction (XRD) patterns at room temperature reveal that all our synthesized samples crystallize in the orthorhombic structure with Pbnm space group. For all samples, the structural data are summarized in Table 1.

| Space group | La$_{0.65}$Ca$_{0.30}$M$_{0.05}$MnO$_3$ M = Na | M = Ag | M = K |
|-------------|------------------------------------------|--------|--------|
| Pbnm        | 5.469(8)                                 | 5.449(1)| 5.455(8)| 5.447(9) |
| Pbnm        | 5.432(5)                                 | 5.483(3)| 5.474(1)| 5.462(7) |
| Pbnm        | 7.740(6)                                 | 7.688(4)| 7.703(2)| 7.739(4) |
| Pbnm        | 230.01                                   | 229.72  | 230.06  | 230.32   |
| $T_C$ (K)   | 248                                      | 295    | 254    | 285     |
| <r$_A$> (Å) | 1.146                                    | 1.149  | 1.154  | 1.165   |
| $\sigma^2$ | 0.36x10$^{-3}$                           | 0.37x10$^{-3}$ | 1.16x10$^{-3}$ | 6.57x10$^{-3}$ |

In this table the average ionic radius <r$_A$> and the mismatch size $\sigma^2$ in the A-site are also listed. The unit cell volume of La$_{0.65}$Ca$_{0.35}$MnO$_3$ (LCMO) sample is found to be 230.01Å$^3$, which is close to that reported by Zhang et al. [10]. The average crystallite size can be estimated using Scherer’s formula: $\langle S \rangle = \frac{K\lambda}{\beta \cos \theta}$, where $\lambda$, $\beta$ and K are the X-ray wave length, the full width at half maximum and the Scherer crystal shape constant respectively [11]. The average crystallite size, ranging between 21nm and 35nm, influences the magnetic and magnetocaloric properties as will be discussed below.

Magnetization measurements versus temperature in the range 20-350K in a magnetic applied field of 50mT showed that all our substituted samples exhibit a sharp transition from paramagnetic to
ferromagnetic state with decreasing temperature (Fig. 1a). The Curie temperature $T_C$, determined from the position of the inflexion point in the $M$ ($T$) curve, is found to be 248K for the parent compound LCMO and 295K, 254K and 285K for M=Na, Ag and K respectively. In order to confirm the ferromagnetic behavior of our samples at low temperatures, we performed magnetization measurements versus magnetic applied field up to 7T at several temperatures. A typical evolution of the magnetization versus magnetic applied field for LCMO sample is plotted in Fig. 1b. Below $T_C$, the magnetization $M$ increases sharply with magnetic applied field for $H<0.5T$ and then saturates above 1T. The saturation magnetization shifts to higher values with decreasing temperature. We plot in Fig. 1c the Arrott curves $M^2(\mu_0H/M)$ for LCMO sample. As can be seen, Arrott plots above $T_C$ show a linear behavior which indicates that a second order magnetic transition occurs. The magnetic entropy change, $|\Delta S_M|$, has been deduced from isothermal magnetization measurements. Based on Maxwell’s relations, $|\Delta S_M|$, can be evaluated using the following equation $|\Delta S_M| = \sum_i \frac{M_i - M_{i+1}}{T_{i+1} - T_i} \Delta H$, 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 $H_i$ [12]. Fig. 1d shows the temperature dependence of the magnetic entropy change, $|\Delta S_M|$, of LCMO sample.

![Fig. 1](image)

**Fig. 1.** a) $M$($T$) at 50mT for $\text{La}_{0.65}\text{Ca}_{0.3}\text{M}_{0.05}\text{MnO}_3$ samples, b) $M$($H$) at several temperatures, c) Arrott curves $M^2(\mu_0H/M)$ and d) $|\Delta S_M|$($T$) at several magnetic applied field for LCMO sample

We can observe that with decreasing temperature, the magnitude of $|\Delta S_M|$ increases progressively up to 235K and then remains roughly constant at low temperatures. The same behaviour has been observed by Pekala et al. [13] on $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ sample prepared by sol-gel method and has been interpreted in terms of nano-crystalline grain size. Figures 2a-c show the temperature dependence of the magnetic entropy change under several magnetic applied fields for $\text{La}_{0.65}\text{Ca}_{0.3}\text{M}_{0.05}\text{MnO}_3$ samples.
(M=Na, Ag, K). All our samples exhibit large MCE effect around the magnetic transition temperature and the magnitude of $|\Delta S_M|$ increases with increasing the magnetic applied field. The maximum magnetic entropy change observed, $|\Delta S_M^{\text{Max}}|$, is found to be $3 \; \text{Jkg}^{-1}\text{K}^{-1}$, $5.16 \; \text{Jkg}^{-1}\text{K}^{-1}$ and $3.54 \; \text{Jkg}^{-1}\text{K}^{-1}$ in a magnetic field change of $5T$ for M=Na, Ag and K respectively. The relative cooling power (RCP) is evaluated as $\text{RCP} = -\Delta S_M(T,H) \times \delta T_{\text{FWHM}}$, where $\delta T_{\text{FWHM}}$ is the full-width at half-maximum of $|\Delta S_M|$ versus temperature [14]. For our samples, the RCP values are respectively $250.3 \; \text{J/kg}$, $279 \; \text{J/kg}$ and $295 \; \text{J/kg}$ at $5T$ for M=Na, Ag and K. The magnitude of the RCP for La$_{0.65}$Ca$_{0.3}$K$_{0.05}$MnO$_3$ specimen is about $72\%$ of that of pure Gd. The higher RCP value is observed in La$_{0.7}$Sr$_{0.3}$MnO$_3$ [15] which reaches $670 \; \text{J/kg}$ under $7T$ around $235 \; \text{K}$ making difficult its application in magnetic refrigeration near room temperature. Moreover La$_{0.7}$Ca$_{0.25}$Sr$_{0.05}$MnO$_3$ [15] and La$_{0.7}$Ca$_{0.2}$Sr$_{0.1}$MnO$_3$ [16] compounds are characterized by an RCP value of $462 \; \text{J/kg}$ (5T) and $374 \; \text{J/kg}$ (5T) respectively around room temperature which are comparable to our results. According to Landau Theory, $|\Delta S_M|$ can be evaluated through the following formula: $\Delta S_M = -\frac{1}{2} \frac{\partial A}{\partial T} M^2 - \frac{1}{4} \frac{\partial B}{\partial T} M^4$ where A and B coefficients are deduced from the linear fit of Arrott plots. Amaral et al. [17] have reported that the calculated value agrees well with the experimental data for La$_{0.7}$Sr$_{0.3}$MnO$_3$ compound, which is known to be a typical system governed by double exchange interaction and is the less affected by other instabilities. We plot in Fig.2d the experimental and calculated curves of $|\Delta S_M|$ as a function of temperature in a magnetic field change of $5T$ for La$_{0.65}$Ca$_{0.3}$K$_{0.05}$MnO$_3$ sample.

![Fig. 2](image)

$|\Delta S_M(T)|$ at several magnetic applied field for a) M=Na, b) M=Ag and c) M=K. d) Experimental and calculated $|\Delta S_M|$ for La$_{0.65}$Ca$_{0.3}$K$_{0.05}$MnO$_3$ sample under 5T.

A shift of 30K to lower values is observed in the calculated curve while the magnitude is four time lager compared to the experimental one. This discrepancy has been also observed by Yang et al. [18]
where the authors compared the theoretical and calculated magnetocaloric effect of electron-doped manganites. This behavior has been explained in terms of Jahn-Teller distortion.

4. Conclusions
We investigated the effect of monovalent doping on the physical properties of La$_{0.65}$Ca$_{0.3}$M$_{0.05}$MnO$_3$ (M=Na, Ag, K) powder samples. The structural study shows that all our synthesized samples crystallize in the orthorhombic structure with Pbnm space group. A large magnetocaloric effect around room temperature is observed in our samples. La$_{0.65}$Ca$_{0.3}$K$_{0.05}$MnO$_3$ exhibits the highest RCP value of 295J/kg in a magnetic applied field change of 5T.

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