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Effect of K doping on the physical properties of $La_{0.65}Ca_{0.35-x}K_xMnO_3$ ($0 \leqslant x \leqslant 0.2$) perovskite manganites

M. Koubaa [a], W. Cheikhrouhou-Koubaa [a], A. Cheikhrouhou [a,b,*]

[a] Laboratoire de Physique des Matériaux, Faculté des Sciences de Sfax, B.P. 1171, 3000 Sfax, Tunisia
[b] Institut NEEL, CNRS, B.P. 166, 38042 Grenoble Cedex 9, France

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ABSTRACT

The effects of K doping in the A-site on the structural, magnetic and magnetocaloric properties in $La_{0.65}Ca_{0.35-x}K_xMnO_3$ ($0 \leqslant x \leqslant 0.2$) powder samples have been investigated. Our samples have been synthesized using the solid-state reaction method at high temperature. The parent compound $La_{0.65}Ca_{0.35}MnO_3$ is an orthorhombic (Pbnm space group) ferromagnet with a Curie temperature T_C of 248 K. X-ray diffraction analysis using the Rietveld refinement show that all our synthesized samples are single phase and crystallize in the orthorhombic structure with Pbnm space group for $x \leqslant 0.1$ and in the rhombohedral system with $R\bar{3}c$ space group for $x = 0.2$ while $La_{0.65}Ca_{0.2}K_{0.15}MnO_3$ sample exhibits both phases with different proportions. 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. Potassium doping leads to an enhancement in the strength of the ferromagnetic double-exchange interaction between Mn ions, and makes the system ferromagnetic at room temperature. Arrott plots show that all our samples exhibit a second-order magnetic-phase transition. The value of the critical exponent, associated with the spontaneous magnetization, decreases from 0.37 for $x = 0.05$ to 0.3 for $x = 0.2$. A large magnetocaloric effect (MCE) has been observed in all samples, the value of the maximum entropy change, $|\Delta S_m|_{max}$, increases from 1.8 J/kg K for $x = 0.05$ to 3.18 J/kg K for $x = 0.2$ under a magnetic field change of 2 T. For $x = 0.15$, the temperature dependence of $|\Delta S_m|$ presents two maxima which may arise from structural inhomogeneity.

1. Introduction

After the discovery of colossal magnetoresistance (CMR), spectacular decrease of resistivity under a magnetic applied field, by Jin et al. [1] in La–Ca–Mn–O epitaxial thin film, the physical properties of the hole-doped manganites $RE_{1-x}M_xMnO_3$ (RE = La, Pr and M = Ca, Sr, Ba) have been investigated intensively [2–4]. Manganites are expected to offer various technical applications such as spintronics-based devices [5,6]. These oxides provide a rich variety of structural, magnetic and transport properties depending on the doping concentration (Mn^{3+}/Mn^{4+} ratio), the average size of the A-site cations $\langle r_A \rangle$ which controls the effective electron bandwidth W and the size mismatch at this A-site [7–10]. The widely studied $La_{1-x}Ca_xMnO_3$ system, which has a relatively intermediate one-electron bandwidth (W), shows at low-temperature ferromagnetic insulator phase for $0.02 \leqslant x \leqslant 0.18$ and ferromagnetic metal phase in the range $0.2 \leqslant x \leqslant 0.5$ [11]. The double-exchange (DE) mechanism between adjacent Mn^{3+} and Mn^{4+} ions has been used first to explain the correlation between magnetic and transport properties [12]. However, both experimental and theoretical studies indicate that DE model alone cannot explain the magneto-transport properties and other factors such as the Jahn–Teller distortion of Mn^{3+} ion (electron–phonon coupling) and phase separation play a key role to understand the CMR physics [13–15].

More recently, an interesting property has been found in the ferromagnetic manganites near the Curie temperature T_C, the magnetocaloric effect (MCE) [16,17]. The origin of this effect is based on the adiabatic demagnetization: the application of a magnetic field in a ferromagnetic material induces a spin reorientation thus decreasing the spin entropy. This process is accompanied by a rise of the lattice entropy when the field is applied adiabatically. On the contrary, if we remove off 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 main requirements for a magnetic material to possess a large magnetic entropy change are the large spontaneous magnetization as well as the sharp drop in the magnetization associated with the

* Corresponding author at: Laboratoire de Physique des Matériaux, Faculté des Sciences de Sfax, B.P. 1171, 3000 Sfax, Tunisia. Tel./fax: +216 74 676607.
E-mail address: abdcheikhrouhou@yahoo.fr (A. Cheikhrouhou).

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ferromagnetic to paramagnetic transition at T_C [18,19]. It has been well-established that the magnitude of the MCE in manganites is comparable to that of pure Gd [20,21]. For $\Delta H = 1.5$ T, both Gd and $La_{2/3}Ca_{1/3}MnO_3$ samples exhibit a maximum magnetic entropy change, $|\Delta S_m|_{max}$, of 4.2 J kg/K at 293 K and 4.3 J kg/K at 253 K, respectively [22]. In order to attain large magnetic entropy changes induced by low magnetic field changes at room temperature, many researchers have reported the effects of partial substitution in the A site of La or Ca by other elements. Hanh et al. [23] found $|\Delta S_m|_{max}$ of 3.72 J/kg K upon a magnetic applied field change of 1.35 T in $La_{0.7}Ca_{0.25}Pb_{0.05}MnO_3$ sample. Zhang et al. [24] investigated the MCE properties in $La_{0.65-x}Eu_xCa_{0.35}MnO_3$ and found that for $x = 0.05$, $|\Delta S_m|_{max}$ reaches 5.78 J/kg K upon a magnetic applied field change of 1.5 T. However, $|\Delta S_m|$ does not extend over a large temperature range as it should be expected in magnetic refrigeration. In the present work, we elaborated by the solid-state method at high temperature the $La_{0.65-x}Ca_{0.35-x}K_xMnO_3$ powder samples and investigated the effect of the potassium substitution on the structural, magnetic and magnetocaloric properties.

2. Experimental techniques

Powder samples of $La_{0.65}Ca_{0.35-x}K_xMnO_3$ ($0 \leqslant x \leqslant 0.2$) were synthesized using the standard solid-state reaction method at high temperature, by mixing La_2O_3, $CaCO_3$, K_2CO_3 and MnO_2 up to 99.9% purity in the desired proportions. 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 (XRD) at room temperature. Structural analysis was carried out using the standard Rietveld technique [25,26]. Magnetization measurements versus temperature in the range 20–350 K and magnetization measurements 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

The X-ray diffraction patterns of all our synthesized $La_{0.65-x}Ca_{0.35-x}K_xMnO_3$ ($0 \leqslant x \leqslant 0.2$) powder samples were recorded at room temperature and based on these patterns, their crystal structures were refined by the Rietveld's profile-fitting method. The experimental diffraction profile was fitted with the pseudo-voigt profile function. 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. It has been found that with increasing K content, our samples undergo a structural phase transition from orthorhombic system with Pbnm space group (for $x \leqslant 0.1$) to rhombohedral system with $R\bar{3}c$ space group (for $x = 0.2$).

The powder pattern of the $La_{0.65}Ca_{0.2}K_{0.15}MnO_3$ ($x = 0.15$) sample can be well reproduced by a combination of orthorhombic Pbnm (90%) and rhombohedral $R\bar{3}c$ (10%) structures. The coexistence at room temperature of these two phases has been also observed by Ulyanov et al. [27] in $La_{0.7}Ca_{0.165}Sr_{0.135}MnO_3$ powder sample. Crystallographic studies performed at room temperature [28] on $La_{0.7}Ca_{0.3-x}Sr_xMnO_3$ ($0 \leqslant x \leqslant 0.33$) samples have shown that for $0.066 \leqslant x \leqslant 0.132$ the system exhibits signature of multi-phasic behavior with no complete splitting into the double line of the fundamental peak in the diffraction profile. Pi et al. [29] have studied the structure of polycrystalline $La_{1-x}Ag_xMnO_3$ samples and have shown the coexistence of both orthorhombic and rhombohedral phases with proportions depending not only on the substitution rate but also on the sintering temperature. Fig. 1 shows typical measured and refined XRD patterns for $x = 0.1$ and 0.15 samples. Based on the consideration of lower χ^2 (goodness-of-fit factor) values, the fit between the experimental spectra and the calculated values is good. Detailed results of the structural parameters deduced from the Rietveld analysis are listed in Table 1. In this table the average ionic radius $\langle r_A \rangle$ and the mismatch size σ^2 of the A-site are also listed. For samples with perovskite structure, it is well known that there are three possible origin of the lattice distortion: (i) the variation of the Mn^{3+}/Mn^{4+}

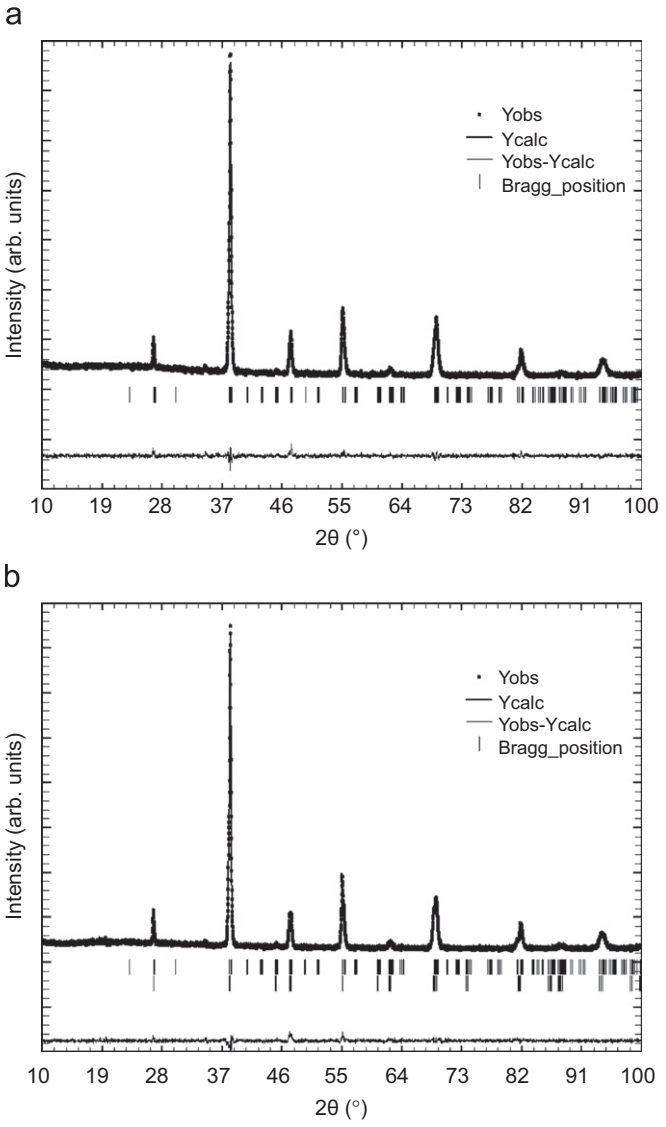

Fig. 1. XRD patterns of (a) $La_{0.65}Ca_{0.25}K_{0.1}MnO_3$ and (b) $La_{0.65}Ca_{0.2}K_{0.15}MnO_3$ compounds. Squares indicate the experimental data and the calculated data is the continuous line overlapping them. The lowest curve shows the difference between experimental and calculated patterns. The vertical bars indicate the expected reflection positions.