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Influence of A-site cation size-disorder on structural, magnetic and magnetocaloric properties of $La_{0.7}Ca_{0.3-x}K_xMnO_3$ compounds

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Abstract

The structural and magnetic properties of perovskite oxides $La_{0.7}Ca_{0.3-x}K_xMnO_3$ ($0 \leq x \leq 0.15$) have been investigated to explore the influence of the A-site cation size-disorder (σ^2). The materials were prepared by the solid-state method and then characterized by X-ray diffraction (XRD). The XRD data have been analyzed by Rietveld refinement technique. For K doping concentration $x \leq 0.075$, the samples crystallize in the orthorhombic structure, while for $x \geq 0.1$, the structure becomes rhombohedral. The variation of the magnetization M as a function of the applied magnetic field $\mu_0 H$ reveals the presence of a structural distortion leading to a reduction of the magnetization at low $\mu_0 H$ values. When increasing $\mu_0 H$, the structural distortion decreases and for a high applied magnetic field, the M ($\mu_0 H$) curves saturate indicating the disappearance of the structural distortion. The influence of K doping concentration and the applied magnetic field on the magnetocaloric properties has been considered. A large magnetic-entropy change ($|\Delta S_M| \sim 5$ J/kg K) is obtained in all samples at Curie temperatures between 270 and 280 K for an applied magnetic field of 3 T. These results show that these materials can be used as candidates for magnetic refrigerants near room temperature.

Keywords: Manganites; Perovskites; Magnetic measurements; Size-disorder; Double-exchange; Orthorhombic distortion; Local distortion; Magnetocaloric effect

1. Introduction

Doped rare-earth manganites with the general formula $R_{1-x}A_xMnO_3$ (R = La, rare-earth, A = Ca, Sr, Ba) have been recently the subject of intense research not only for their colossal magnetoresistance (CMR) effects but also for the large magnetocaloric effects that certain ferromagnetic manganites exhibit [1–5]. As a function of temperature, applied magnetic field, doping concentration x, A-site ionic radius $\langle r_A \rangle$, and A-site size-disorder, this system displays a rich phase diagram for both structural and magnetic properties. A large family of manganese perovskites thus exists and among them the parent compound $LaMnO_3$ order antiferromagnetically owing to the super-exchange antiferromagnetic interaction between Mn^{3+} ions. As A^{2+} is substituted for La^{3+}, charge conservation requires Mn^{3+} conversion to Mn^{4+} ions. Then a new magnetic interaction comes into view, the double-exchange (DE) interaction [6]. It basically consists of transfer of an electron between neighbouring Mn^{3+} and Mn^{4+} ions through the path Mn–O–Mn resulting in an effective ferromagnetic interaction due to the strong on-site Hund's coupling. It is believed that this DE interaction controls magnetic and electrical properties of perovskites manganites. However, numerous experimental results suggest that the DE model could not alone explain the entire behaviour of these materials. It is proved that other considerations, such as the coupling between spin and orbital structure [7] and the Jahn–Teller (JT) distortions [8], influence the structural and magnetic properties of these materials. The JT lattice distortion is found to be larger in the paramagnetic phase.

The size of the substitutional ion is a key factor influencing the different properties of manganites. It has been shown that these properties depend on the mean size of cations at the A-site $\langle r_A \rangle$ [9] and the disorder resulting from the A-site cation size mismatch σ^2 [10]. The structural disorder produces a strong local stress in MnO_6 octahedra (resulting in rotation), modifying

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the Mn–O–Mn angles and thus changing lattice and electronic properties.

Recently, many studies of manganites doped with divalent ion have been reported [11,12]. However, there is substantially less information in literature regarding the substitution in the A-site with a monovalent ion [13,14].

The aim of this work was to study the effect of monovalent K^+ ion substitution for divalent Ca^{2+} ion on the structural, magnetic and magnetocaloric properties of $La_{0.7}Ca_{0.3-x}K_xMnO_3$ compounds. We also demonstrate the relationship between the applied magnetic field μ_0H and the A-site cation size mismatch σ^2.

2. Experimental details

Polycrystalline samples of $La_{0.7}Ca_{0.3-x}K_xMnO_3$ were prepared by the reaction of stoichiometric amounts of La_2O_3, K_2CO_3, $CaCO_3$ and MnO_2 powders in the solid state. The mixture was initially heated at 1173 K for 3 days followed by subsequently heating at higher temperatures with intermediate grindings, until monophasic powder was obtained. Then, the powder was pressed into pellets forms under 4 tonnes/cm^2 and sintered at 1673 K for 1 day in air with several periods of grinding and repelleting. Finally, these pellets were rapidly quenched to room temperature. This step was made in order to keep the structure at an annealed temperature.

The structure of the samples was characterized by powder X-ray diffraction with Mo radiation ($\lambda = 0.709362$ Å) by step scanning (0.02°). The data were analyzed by the Rietveld method using the FULLPROF program [15].

Magnetic measurements, the dependence of magnetization on the temperature and applied external field, were carried out by using a Foner magnetometer (FON). Magnetization of the sample was measured in an isothermal regime under an applied magnetic field varying from 0 to 10 T. The range of temperature for isotherm M versus μ_0H measurements was fixed around the transition temperature of the sample (T_C). This temperature was previously determined from $M(T)$ curves, and coincides with the temperature at which a maximum of $\partial M/\partial T$ is observed. Isothermal M versus μ_0H curves were collected by steps every 2 K. The magnetic-entropy changes, ΔS_M, were calculated from the magnetization data, which is based on a Maxwell relation.

3. Results and discussion

It is clear from the diffraction pattern that the synthesized compounds are single phase. Fig. 1 shows the refinement of $La_{0.7}Ca_{0.3-x}K_xMnO_3$ samples ($x = 0.05$ and 0.10). Refined cell parameters, unit cell volume, mean ionic radii $\langle r_A \rangle$ and selected interatomic distances and angles are given in Table 1. The goodness-of-fit parameters given by this program contains the weighted pattern R_{wp}, the pattern R_p and the goodness of fit χ^2. It was found that samples with $0 \le x \le 0.075$ show an orthorhombic structure in the $Pnma$ space group. The structure refinement of samples with 10 and 15% potassium was performed in the hexagonal setting of $R\bar{3}c$ space group.

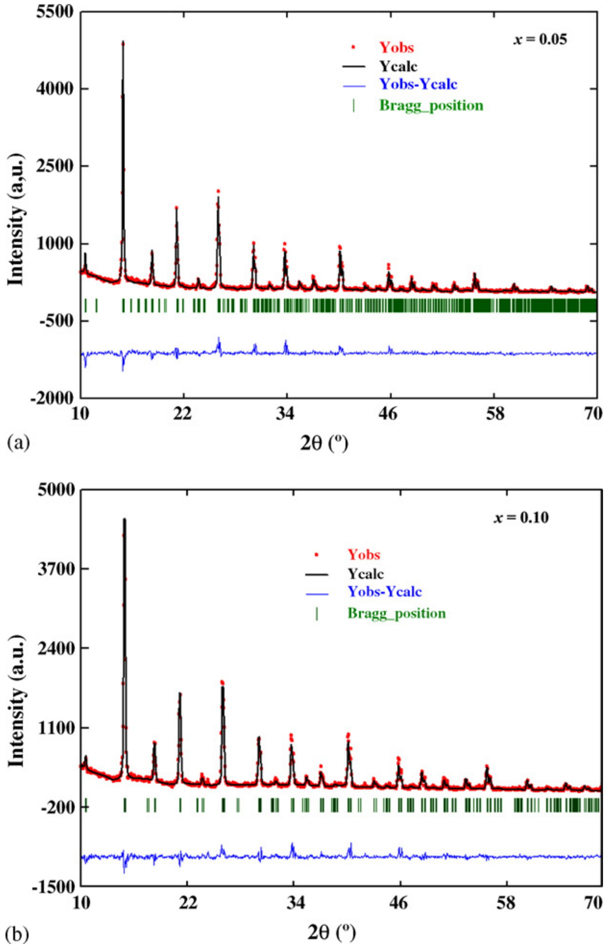

Fig. 1. Observed (circle), calculated (continuous line) and difference patterns (at the bottom) of X-ray diffraction data: (a) $x = 0.05$ (orthorhombic structure, $Pnma$), (b) $x = 0.10$ (rhombohedral structure, $R\bar{3}c$) in $La_{0.7}Ca_{0.3-x}K_xMnO_3$ compounds. The vertical tick indicates the allowed reflections.

Table 1
Structural parameters, selected interatomic distances and angles in $La_{0.7}Ca_{0.3-x}K_xMnO_3$ compounds determined from FULLPROF refinements to XRD powder diffraction data

x	0.000	0.050	0.075	0.100	0.150
Space group	$Pnma$	$Pnma$	$Pnma$	$R\bar{3}c$	$R\bar{3}c$
a (Å)	5.4734_2	5.4648_9	5.4617_7	5.4662_4	5.4666_3
b (Å)	5.4807_6	5.4829_4	5.4620_5		
c (Å)	7.7615_8	7.7301_1	7.7333_4		
α				60.0828_2	60.0977_7
Unit cell volume V (Å^3)	58.209_3	57.905_5	57.676_2	57.861_5	57.905_1
$\theta_{Mn-O(1)-Mn}$ (°)	163.37_6	166.47_2	171.09_2	168.95_4	165.06_6
$d_{Mn-O(1)}$ (Å)	1.961_0	1.946_8	1.939_2	1.942_9	1.950_6
R_{wp} (%)	8.72	12.3	10.5	11.1	10.2
R_p (%)	6.42	9.52	8.07	8.68	8.26
χ^2 (%)	3.91	3.00	3.05	2.55	4.05
$\langle r_A \rangle$ (Å)	1.205	1.223	1.233	1.242	1.260