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Structural, magnetic and magnetocaloric properties of $La_{0.7}Ca_{0.2}Sr_{0.1}Mn_{1-x}Cr_xO_3$ compounds with $x = 0$, 0.05 and 0.1

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ABSTRACT

Structural, magnetic and magnetocaloric properties of $La_{0.7}Sr_{0.1}Ca_{0.2}Mn_{1-x}Cr_xO_3$ compounds with $x = 0$, 0.05 and 0.1 have been investigated to shed light on Cr-doping influence. X-ray diffraction studies show that all samples crystallize in the rhombohedral symmetry with $R\bar{3}c$ space group. Rietveld refinement structure shows that the insertion of Cr in Mn network modifies the structural parameters such as the volume, Mn–O–Mn angles and the Mn–O bond length. The substitution of Mn by Cr decreases the 2p-3d hybridization between O and Mn ions, reduces the bandwidth and increases the electron–phonon coupling. The investigation of magnetic and magnetocaloric properties reveals that the samples exhibit a paramagnetic(PM)–ferromagnetic (FM) transition with decreasing Curie temperature (T_C) from 294 K to 255 K when Cr doping level increases. The magnetic entropy change (ΔS_M^{max}) also decreases from 6.20 J kg^{-1} K^{-1} for $x = 0$ to3.80 J kg^{-1} K^{-1} for $x = 0.1$, while the relative cooling power (RCP) increases from 234.5 to 240 J kg^{-1}, respectively, under a magnetic field of 5 T. These outcomes suggest that Mn-site Cr doping inhibits the enhancement of the magnetocaloric effect in some perovskite manganites. This is explained by the weakening of the ferromagnetic double-exchange interaction between Mn^{3+} and Mn^{4+} ions.

1. Introduction

The manganites with the form of $(RE^{3+}_{1-x}M^{2+}_x)$ MnO_3 (RE = trivalent rare earth, M = divalent alkaline earth) have attracted much attention over the past few years due to their extraordinary magnetic and electronic properties, as well as for being very promising for future technological applications [1–3]. The importance of these materials lies in the fact that they are insulator–metal transition together with a paramagnetic(PM)–ferromagnetic(FM) transition and having colossal magnetoresistance (CMR) effect. This has been extensively explained in the framework involving double exchange model and Jahn–Teller effects [4,5]. Besides the CMR effect which has potential applications in information storage and magnetic sensors, these materials have also been found to exhibit the magnetocaloric effect (MCE) under a moderate applied magnetic field. The recent development of new magnetic refrigeration (MR) technology, which is based upon the MCE, has brought about an alternative to the conventional gas compression (CGC) technique. An interest in perovskite-type manganese oxides has recently been prompted by the observation of CMR. These materials present some advantages compared to Gd and inter-metallic alloys. These advantages include low production cost, chemical stability, high resistivity [6] and corrosion-free effect. Consequently manganites have attracted more attention as alternative candidates for magnetic refrigeration in the vicinity of room temperature. Among these, perovskite manganites are of special interest as they are known to possess interesting fundamental properties with potential device applicability. When the Re site is doped with a divalent ion, a proportional number of Mn^{3+} ions are converted into Mn^{4+} ions and mobile e_g electrons are introduced; which has led to mediating the ferromagnetic interaction according to a double exchange between Mn^{3+} and Mn^{4+} with electronic configuration $\left(3d^4, t_{2g}^3 \uparrow e_g^1, S = 2\right)$ and $\left(3d^3, t_{2g}^3 \uparrow e_g^0, S = 3/2\right)$ respectively. The magnetic properties of $RE_{1-x}M_xMnO_3$ phases are strongly affected by the Mn–O bond length and Mn–O–Mn bond angle controlled by the ionic radii of A and B site ions and Mn^{3+}/Mn^{4+} ratio which modifies the double exchange and super exchange interactions [7]. The magnetic and transport properties of the system are then determined by the competition between the double exchange and super exchange interactions. In order to understand the unusual structure, magnetic and magnetocaloric effect properties of

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doped perovskites $RE_{1-x}M_xMnO_3$, many studies have been carried out by doping the trivalent rare earth site (A-site) with divalent atoms (Ca, Ba, Sr, etc.) [8–10]. Other studies have also shown that the substitution of Mn (B-site) dramatically affects the structure, magnetic and magnetocaloric effect properties [11,12]. The B site modification has a merit in that it directly affects the Mn network by changing the Mn^{3+}/Mn^{4+} ratio and the electron carrier density. Therefore, in order to better understand the role of Mn and its local environment in $La_{0.7}Ca_{0.2}Sr_{0.1}MnO_3$, we studied the effect of replacing some of the Mn with Cr. The choice of the ion Cr^{3+} is based on the fact that its electronic structure is the same as Mn^{4+} $\left(3d^3, t_{2g}^3 \uparrow e_g^0, S = 3/2\right)$ and its ionic radius (0.615 Å) is smaller than that of the Mn^{3+}(0.645 Å). There may be FM DE interaction between Cr^{3+} and Mn^{3+} similar to that between Mn^{4+} and Mn^{3+}. The main goal of this work is to study the effect of Cr doping on the structural, magnetic and magnetocaloric properties of $La_{0.7}Ca_{0.2}Sr_{0.1}Mn_{1-x}Cr_x\ O_3$ $(0 \leqslant x \leqslant 1)$ compounds. These compounds were investigated by X-ray diffraction, magnetization and magnetocaloric measurements. The second objective of this work is to find a new compound, which can broaden the temperature range of magnetic refrigeration.

2. Experimental procedures

$La_{0.7}Ca_{0.2}Sr_{0.1}Mn_{1-x}Cr_xO_3$ $(0 \leqslant x \leqslant 0.1)$($LCSM_{1-x}Cr_xO$) samples were prepared by mixing stoichiometric quantities of La_2O_3, $SrCO_3$, $CaCO_3$, MnO_2 and Cr_2O_3 (at least 99.99% in purity) in ambient atmosphere using the conventional solid-state reaction method. These compounds were heated in air on two steps (1000 °C for 48 h, 1200 °C for 24 h) and pressed into disks. Intermediate grindings were made. Pellets were finally annealed at 1400 °C for 24 h and cooled down to room temperature.

The structure and purity phase of the samples were checked at room temperature by means of X-ray powder diffraction (XRD) using Cu Kα radiation (λ = 1.5406 Å). The data collection was performed by step-scan modes, in a 2θ range between 10° and 100° with step-size of 0.017° and step time of 18 s. The structural parameters were obtained by fitting the experimental data of XRD using the Rietveld structural refinement program FULLPROF soft-ware (Version 1.9c-May 2001-LLB-JRC) [13].

Magnetization (M) vs. temperature (T) and magnetization vs. magnetic field ($\mu_0 H$) were measured using a magnetometer in Aveiro University.

3. Result and discussion

3.1. X-ray analysis

The XRD patterns of the illustrated samples in Fig. 1 present sharp and intense peaks corresponding to the perovskite phase. All the samples are single phase, without a detectable secondary phase within the sensitivity limits of the experiment (a few percent). The structure refinement was performed in the hexagonal setting of the rhombohedral $R\bar{3}c$ ($Z = 6$) space group, in which (La, Sr, Ca) at 6a (0, 0, 0.25) position, (Mn, Cr) at 6b (0, 0, 0), and O at 18e (x, 0, 0.25). The inset of Fig. 1 exemplifies the Rietveld refinement for $x = 0$ compound showing a good agreement between observed and calculated profiles. Detailed results of the refinement are listed in Table 1; particularly the refined occupancy factor of (Mn/Cr) is close to the nominal one. The lattice size is slightly contracted with increasing Cr doping concentration, indicating that the Mn^{3+}cations are mainly replaced by the Cr^{3+} ions. This provides a reasonable description of the decrease in the lattice volume with the Cr doping because the radius of Cr^{3+} ion (r_{Cr}^{3+} = 0.615 Å) is slightly smaller than that of Mn^{3+} (r_{Mn}^{3+} = 0.645 Å) but much larger than that of Mn^{4+} (r_{Mn}^{4+} = 0.53 Å) [14]. This fact makes the (Mn, Cr)–O–(Mn, Cr) bond angle decreases, which affects the transfer integral b_{ij} of the e_g electrons and the on-site exchange interaction (Hund's rule coupling, J_h) between the itinerant e_g electrons and the localized t_{2g} spins ($S = 3/2$) of Mn^{3+} and Cr^{3+}ions. It has been reported that the deformation of the MnO_6 octahedra may be required to account for lattice distortion of the perovskite structures. Nevertheless, the average ionic radius of A-site is fixed in the investigated samples. Accordingly, the lattice distortion is caused by the partial replacement of Mn by Cr which is governed by the tolerance factor $\left(t = \frac{r_{(La,Sr,Ca)} + r_O}{\sqrt{2}\left(r_{(Mn,Cr)} + r_O\right)}\right)$, which is the geometric measure of size mismatch of the perovskites. The tolerance factor (t) increases linearly from 0.9208 to 0.9222 for $La_{0.7}Ca_{0.2}Sr_{0.1}MnO_3$ and $La_{0.7}Ca_{0.2}Sr_{0.1}Mn_{0.9}Cr_{0.1}O_3$, respectively, which is the stable range of the perovskite structure $0.89 < t < 1.02$ [15].

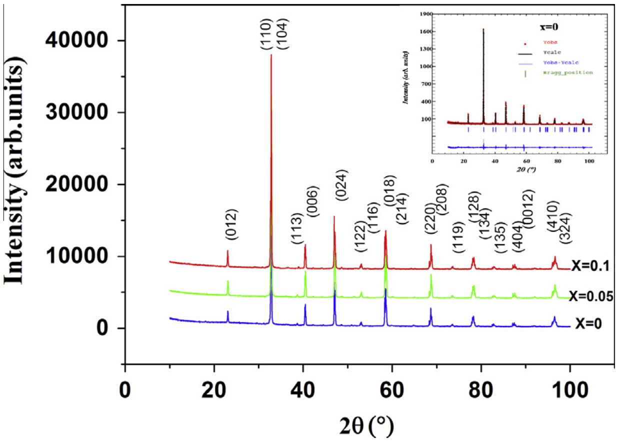

Fig. 1. X-ray diffraction patterns of $La_{0.7}Ca_{0.2}Sr_{0.1}Mn_{1-x}Cr_x\ O_3$ $(0 \leqslant x \leqslant 0.1)$ compounds at room temperature. All peaks of the manganite phase are indexed in the rhombohedra R-3c symmetry. The inset shows observed (symbol) and calculated (solid line) XRD patterns obtained by the Rietveld analysis for $x = 0.0$ manganite. Their difference (enlarged scale) is represented at the bottom of the figure (solid line). The vertical ticks show the positions of the calculated Bragg reflections for the rhombohedric phase (R-3c space group).

In the present investigation, as (t) values are increasing continuously by doping with smaller ions, it is logical to conclude that there is a decrease in the structural distortion. This distortion does not only change the lattice symmetry, but also modifies the cell deformation [16].

The average crystallite size values have been estimated from the full width at half maximum of X-ray diffraction peaks. The effects of synthesis, instrumental and processing conditions have been taken with care while making the calculation of crystallite sizes. The broadening of Bragg reflections due to micro strains was considered to have angular dependence and is given by: $\beta_{strain} = 4\varepsilon \tan\theta$ here β_{strain} is the peak shift due to the strain,

Table 1
Results of Rietveld refinements, determined from XRD patterns measured at room temperature for $La_{0.7}Ca_{0.2}Sr_{0.1}Mn_{1-x}Cr_x\ O_3$ $(0 \leqslant x \leqslant 0.1)$.

Compounds	$LCSMnO_3$	$LCSMCr_{0.05}$	$LCSMCr_{0.1}$
$R\bar{3}c$ phase			
a (Å)	5.4836 (5)	5.4807 (2)	5.4802 (2)
c (Å)	13.3929 (1)	13.3812 (3)	13.3759 (6)
V (Å^3)	348.77 (1)	348.09 (5)	347.89 (1)
B_{iso} (Å^2) (La/Ca/Sr)	1.02 (1)	0.54 (2)	1.22 (3)
B_{iso} (Å^2) (Mn/Cr)	0.44 (3)	0.32 (5)	0.43 (3)
x (O)	0.559 (4)	0.545 (5)	0.539 (6)
B_{iso} (Å^2) (O)	1.68 (3)	1.35 (2)	1.77 (1)
Bond lengths and bond angles			
$\langle d_{Mn-O} \rangle$ (Å)	1.952 (3)	1.955 (1)	1.958 (4)
$\langle \theta_{Mn-O-Mn} \rangle$ (°)	165.6 (1)	164.48 (5)	162.9 (2)
Discrepancy factors			
R_P (%)	4.73	4.12	4.54
R_{wp} (%)	6.51	6.63	7.12
R_F (%)	5.97	2.89	5.21
X^2	2.54	1.72	2.93

Space group ($R\bar{3}c$). The atomic positions are 6a (0, 0, 0.25) for (La, Ca, Sr); 6b (0, 0, 0) for (Mn, Cr); 18e (x, 0, 0.25) for oxygen.