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Structural, magnetic and magnetocaloric properties of Ag-doped $La_{0.5}Ca_{0.5-x}Ag_xMnO_3$ compounds with $0 \leqslant x \leqslant 0.4$

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ABSTRACT

Structural, magnetic and magnetocaloric properties of manganites series with the $La_{0.5}Ca_{0.5-x}Ag_xMnO_3$ ($0.0 \leqslant x \leqslant 0.4$) compounds were investigated. Samples were synthesized using the solid state reaction at high temperature and analyzed by XRD data based on the Rietveld refinement technique. Samples with $x = 0.0$, 0.1, 0.2, 0.3 and 0.4 crystallized in orthorhombic symmetry with *Pnma* space group. Also, Magnetizations measurements were performed to investigate magnetic properties. Transition from ferromagnetic (FM) to charge ordered antiferromagnetic (CO-AFM) phases at low temperature is observed for Ag-free $La_{0.5}Ca_{0.5}MnO_3$. Compounds with $x = 0.2$, 0.3 and 0.4, do not exhibit this transition, and only FM metallic phases are observed. The Curie temperature T_C increases with increasing Ag amount from 222 K (for $x = 0.0$) to 264 K (for $x = 0.2$).While $x > 0.2$, T_C remains substantially constant. Magnetic entropy change (ΔS_M) was estimated from isothermal magnetization data. Parent compound ($x = 0.0$) exhibits both normal (negative ΔS_M) and inverse (positive ΔS_M) magnetocaloric effects at T_C and T_{CO}, respectively. However, all the Ag doped samples show only normal magnetocaloric effect at T_C. The Largest MCE occurs for sample with $x = 0.4$ ($\Delta S_M = 3.27\ \mathrm{J\,kg^{-1}\,K^{-1}}$, $\Delta H = 5$ T) for which largest relative cooling power ($RCP = 229.27\ \mathrm{J\,kg^{-1}}$, $\Delta H = 5$ T) is reached as well.

1. Introduction

Magnetic refrigeration is becoming a promising technology to replace the conventional gas-compression refrigeration due to its high efficiency, small volume, energy saving and ecological cleanliness [1,2]. MR is based on the magnetocaloric effect that is, an isothermal magnetic entropy change ($-\Delta S_M$) or an adiabatic temperature change of the magnetic refrigerants. This makes MCE interesting for basic research and investigation of its possible technological application [3]. So, much attention is being paid to find new series of substituted perovskites with the largest possible magnetocaloric effect (comparable to Gd and $Gd_5Ge_2Si_2$) [1]. The manganite system $R_{1-x}A_xMnO_3$, where A is a divalent cation (such as Ca, Sr, and Ba) and *R* is a trivalent rare earth metal, exhibit interesting properties manifested by complex phase diagrams which can be tuned by doping, internal/external pressure, electric and magnetic fields [4,5]. Metallic-insulating transitions depending on these parameters can be observed by this material type. For the classic $La_{1-x}Ca_xMnO_3$ system, the reference state ($x = 0.0$) is an antiferromagnetic insulator while a ferromagnetic conducting state take place for $x \approx 0.2$–0.5 and for $x > 0.5$ antiferromagnetic insulating phases are found. According to these interesting properties, electron–electron and electron phonon interactions should be considered [6].Namely, the half doped perovskite manganites $Ln_{0.5}A_{0.5}MnO_3$ (Ln = rare earth, A = alkaline earth) attract great attention because they display rich physics including charge ordering (CO) and orbital ordering (OO) [7,8]. Investigations of charge ordering in the rare earth manganites have revealed extraordinary variety in the properties including their sensitivity to external factors such as the average size of the A-site cations, magnetic and electrical fields, hydrostatic pressure, as well as isotopic and chemical substitutions [7,9]. For example, the substitution of Mn by Cr or Co can significantly affect the stability of the CO phase and leads to the coexistence of the CO state and the ferromagnetic (FM) metallic state associated with the double-exchange (DE) mechanism [10,11].

$La_{0.5}Ca_{0.5}MnO_3$ is a typical system showing CO phenomena. It undergoes a paramagnetic (PM) to ferromagnetic (FM) transition at $T_C \sim 225$ K, which is followed by a transition to a charge ordered state with a CE-type antiferromagnetic (AFM) magnetic structure at $T_{CO} \sim 150$ K during cooling sequence ($T_{CO} \sim 200$ K on warming) [12]. Further recent studies indicate that kinetic hindrance to this first order transition has serious consequences on the coexisting phases [13,14]. It is widely believed that the properties of manganese oxides are mainly determined by the Mn^{3+}/Mn^{4+} ratio and the Mn–O–Mn bond angle, which affects the orbital overlapping

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between neighboring ions [7].Therefore, it is very interesting to investigate the structure, transport and magnetic properties in the compound $La_{0.5}Ca_{0.5}MnO_3$ in which a tetravalent element is partially substituted at La sites. The motivation for the present study in the perovskite manganites stems from the possible utility of colossal magnetoresistance (CMR) effect and large magnetocaloric (MC) properties at low field and room temperature. Tang et al. studied CMR and MC effect in series of bulk perovskites manganites $LaAgMnO_3$ and they found giant magnetoresistance of 25.5% at room temperature and magnetic entropy change larger than that of gadolinium [15,16].Thus, it is possible to use them as the magnetic refrigerants working in quite a large temperature range. From this view-point, this paper reports the effect of silver substitution on structural, magnetic and magnetocaloric properties in $La_{0.5}Ca_{0.5}MnO_3$ with compositional formula $La_{0.5}Ca_{0.5-x}Ag_xMnO_3$ ($x = 0$, 0.1, 0.2, 0.3 and 0.4).

2. Experimental techniques

The powder samples $La_{0.5}Ca_{0.5-x}Ag_xMnO_3$ ($x = 0$, 0.1, 0.2, 0.3 and 0.4) were prepared using the conventional solid state reaction method at high temperature. Stoichiometric quantities of dried La_2O_3, $CaCO_3$, MnO_2 and Ag_2O were mixed and fired at 700 °C for 24 h, all precursors with purity better than 99.9%. The mixture was pressed and heated in air several times with intermediate grinding. Phase purity and homogeneity were determined by X-ray diffraction (XRD) (Cu Kα radiation $\lambda_{Cu} = 1.5406$ Å) at room temperature. Structural analysis was carried out using the standard Rietveld technique [17].The average of Mn^{3+} and Mn^{4+} ions was checked by a manganimetric titration. Magnetization measurements versus temperature and versus magnetic applied field were carried out using a superconducting quantum interference device (SQUID) magnetometer in the temperature range 5–300 K and up to 5 T.

3. Results and discussion

3.1. Chemical analysis

As samples have been elaborated in air, they are consequently stoichiometric in oxygen [18]. For our samples the Mn^{4+}/Mn^{3+} amount is theoretically equal to one, however the average ion radius of the A cation site $\langle r_A \rangle$ and the cationic disorder σ^2 change. The Mn^{4+} and Mn^{3+} contents have been checked by chemical analysis. We list in Table 1 the chemical analysis results. The experimental analysis results show that the Mn^{4+} content for our samples are slightly smaller than the theoretical values. The ratio Mn^{4+}/Mn^{3+} is equal to 0.95 for the parent compound and 1.46, 2.35 for $La_{0.5}Ca_{0.4}Ag_{0.1}MnO_3$ and $La_{0.5}Ca_{0.3}Ag_{0.2}MnO_3$ samples, respectively. For $x > 0.2$, the results of tests indicate that the Mn^{4+} content for our samples are lower than the theoretical values. Relative error is large due to the existence of secondary phases

Table 1
Chemical analysis results for $La_{0.5}Ca_{0.5-x}Ag_xMnO_3$samples ($x = 0.0$, 0.1, 0.2, 0.3 and 0.4).

Theoretical contents			Experimental contents		
Rate of Silver	Mn^{3+}(%)	Mn^{4+}(%)	Mn^{3+}(%)	Mn^{4+}(%)	ΔMn^{4+}(%)
0.0	50	50	51.33	48.61	−2.78
0.1	40	60	40.62	59.62	−0.63
0.2	30	70	29.77	69.98	−0.03
0.3	20	80	28.69	71.16	−11.05
0.4	10	90	31.96	68.04	−24.40

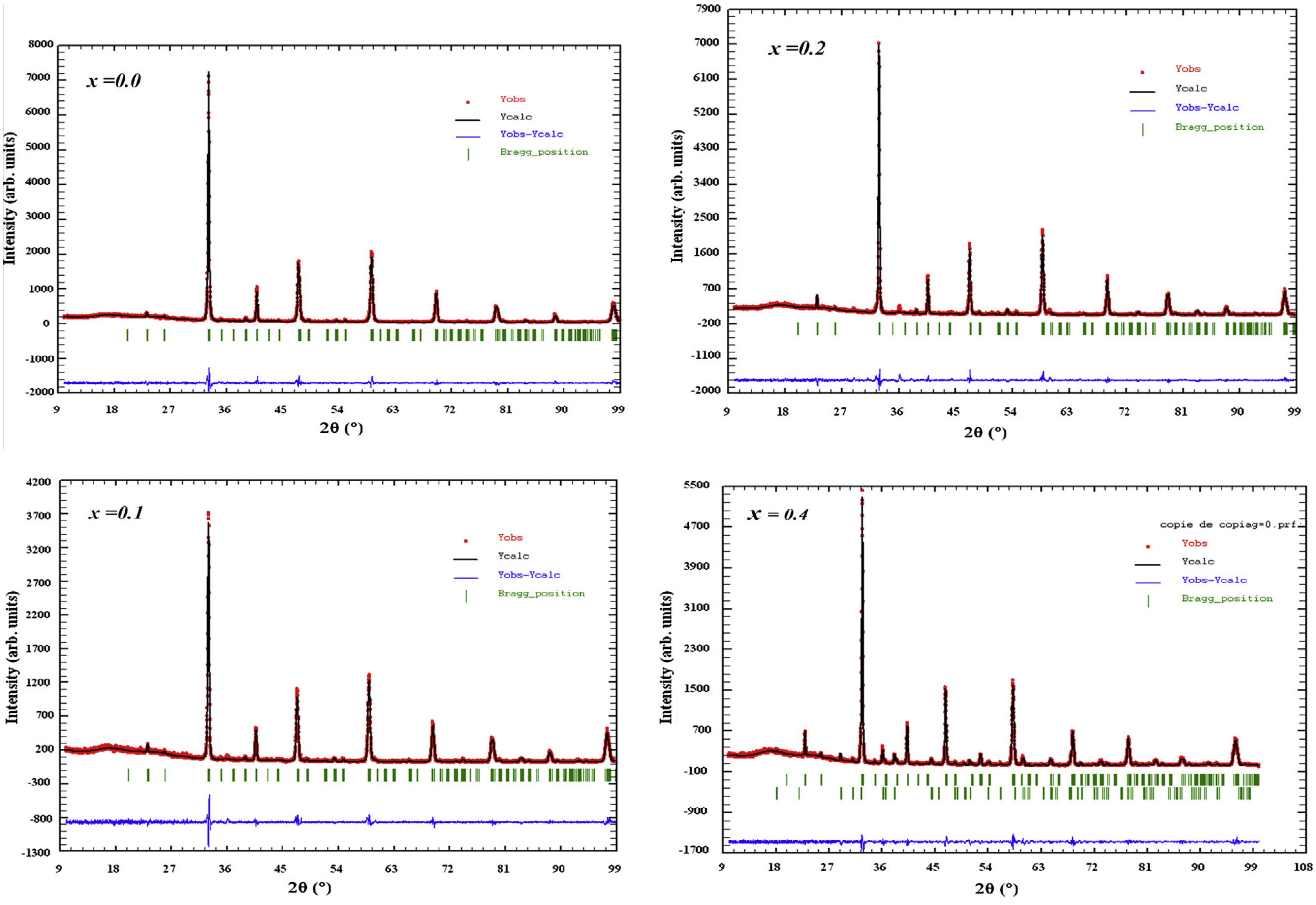

Fig. 1. XRD patterns of $La_{0.5}Ca_{0.5-x}Ag_xMnO_3$ ($x = 0.0$, 0.1, 0.2 and 0.4).