

The effect of the B-site size on the structural, magnetic and electrical properties of $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_{3-\delta}$ compounds

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Abstract

The perovskite-type ceramic $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_{3-\delta}$ was prepared by the solid-state reaction with $0.00 \leq \delta \leq 0.15$. X-ray diffraction, electrical and magnetic measurements were performed to examine the effect of the B-site size on the properties of these materials. We have found that the structure is orthorhombic for $0.00 \leq \delta \leq 0.075$ and becomes rhombohedral for $0.10 \leq \delta \leq 0.15$. The measurements of the magnetization as a function of the temperature, $M(T)$, shows a ferromagnetic-paramagnetic transition at the Curie temperature T_C for $\delta = 0.00$. When increasing δ , these curves report the presence of two types of transitions. The first one is from the ferromagnetic to the antiferromagnetic state, indicating the existence of a charge-ordering state (T_{CO}). The second antiferromagnetic-paramagnetic transition occurs at the Neel temperature T_N . The temperature dependence of the resistivity $\rho(T)$, indicates a metallic behaviour at low temperature ($T < T_p$) and a semiconductor behaviour at high temperature ($T > T_p$) for $\delta = 0.00$. For $0.05 \leq \delta \leq 0.10$, the $\rho(T)$ curves shows a semiconductor behaviour revealing the disappearance of the metallic state which reappear at low temperature for $\delta = 0.125$ and 0.150 . © 2006 Elsevier B.V. All rights reserved.

Keywords: Manganites; Ferromagnetic; Double-exchange; Super exchange; Charge-ordering; Jahn–Teller effect

1. Introduction

The perovskite manganites $\text{La}_{1-x}\text{A}_x\text{MnO}_3$ (A = divalent alkali element such as Ca, Sr and Ba) have attracted a considerable attention, in recent years, to studying the interplay between structure, magnetism and electronic properties [1–5]. The mixed valence $\text{Mn}^{3+}/\text{Mn}^{4+}$ is a key factor to understand the rich physics of manganites, which is governed by the relationship between charge and orbital degrees of freedom. The studies of the $\text{La}_{1-x}\text{A}_x\text{MnO}_3$ compounds have highlighted the important role played by the size of the A-site cations $\langle r_A \rangle$ in determining the properties of these materials [6,7]. Also, $\langle r_A \rangle$ has been shown to influence the magnetic transition temperatures and the nature of charge ordering [8,9]. There is substantially less information regarding the B-site size effect.

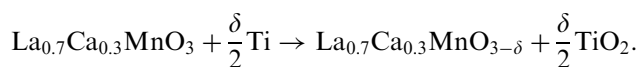
In order to study the influence of the mean size of the B-site, we investigated the crystal structure, magnetic and

electrical properties of $\text{La}_{0.7}^{3+}\text{Ca}_{0.3}^{2+}\text{Mn}_{0.7+2\delta}^{3+}\text{Mn}_{0.3-2\delta}^{4+}\text{O}_{3-\delta}^{2-}$ compounds $0 \leq \delta \leq 0.15$.

2. Experimental

Polycrystalline samples of $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ were synthesized by solid-state reaction. Stoichiometric La_2O_3 , CaCO_3 and MnO_2 powders were mixed and then calcined at 1100 K for several times with intermediate grinding. Finally, the powder was sintered at 1673 K for 48 h and slow cooled to the room temperature.

In order to create vacancies in oxygen sites, the parent oxide was placed in a quartz tube containing titanium in stoichiometric proportion according to the following reaction:



In order to control the reaction, the products obtained are weighted. These weights allow us to determine the real rate of the created oxygen vacancies.

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3. Results and discussion

3.1. Structural characterization

The X-ray diffraction (XRD) analysis with CrK_{α} radiation at room temperature confirmed single-phase composition of the studied samples. The least squares calculations revealed an orthorhombic structure for $0 \leq \delta \leq 0.075$, while for $0.10 \leq \delta \leq 0.15$ the structure becomes rhombohedral (Fig. 1).

Table 1 illustrates the crystallographic data for $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_{3-\delta}$ compounds. The increase of δ , converts $2\delta \text{ Mn}^{4+}$ ions to Mn^{3+} , which have a strong Jahn–Teller (JT) character, then a cooperative JT distortion ($c/a < \sqrt{2}$) of the MnO_6 octahedra increases due to the ordering of the $\text{Mn}^{3+} e_g$ orbital [10]. This orbital ordering produces a strong local stress in MnO_6 octahedra, which modifies the Mn–O–Mn angles.

The variation of the Mn–O–Mn bond angle as a function of δ and the contents of Mn^{3+} ions is shown in Fig. 2, indicates that this variation is pronounced for the orthorhombic structure and is reduced in the compounds with the rhombohedral structure.

For $\delta \geq 0.10$, the local deformation of the structure becomes very important which induces a transition from the orthorhombic to the rhombohedral structure.

The evolution of the unit cell volume V shown in Fig. 3 reveals an increase of the volume V when the size of cations at B-site $\langle r_B \rangle$ increases, which can be explained by the increase of the content of Mn^{3+} ions characterized by a larger ionic radius than Mn^{4+} ($r(\text{Mn}^{3+}) = 0.65 \text{ \AA}$ [11]; $r(\text{Mn}^{4+}) = 0.53 \text{ \AA}$ [12]).

3.2. Magnetic and electrical properties

The temperature dependence of the resistivity (ρ) and the magnetization (M) of $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_{3-\delta}$ samples are shown in Fig. 4. The $M(T)$ measurements displayed are warming curves at 500 Oe.

For $\delta = 0.00$, sample is ferromagnetic (FM) and a ferromagnetic- paramagnetic transition occurs at the Curie temperature T_C defined as a maximum in dM/dT curve. Concurrently, the sample exhibit a metallic behaviour ($d\rho/dT > 0$) at low temperature ($T < T_P$) and a semiconductor character when $T > T_P$, where T_P is defined as the maximum of the resistivity. In the low-temperature FM regime, the temperature dependence of the resistivity can be described as a quadratic function of temperature $\rho(T) = \rho(0) + AT^2$ (Fig. 5).

The nature of the low-temperature ferromagnetic metal phase, and the coupling between T_C and T_P , were discussed in 1951 by Zener [13] who proposed the double-exchange mechanism. It basically consists of the transfer of an electron between neighbouring Mn^{3+} and Mn^{4+} ions through the path Mn–O–Mn. This results in an effective FM interaction due to the strong onsite Hund’s coupling. The magnetic and transport properties of double-exchange ferromagnets are controlled by the one-electron bandwidth W , which is characterized by the overlap between the Mn(3d) and O(2p) orbital, is given by [14]:

$$W \sim \frac{\cos[1/2(\pi - \gamma)]}{(d_{\text{Mn-O}})^{3.5}},$$

where γ is the Mn–O–Mn bond angle and $d_{\text{Mn-O}}$ is the Mn–O bond length.

The bandwidth can be effectively tuned by the “internal” pressure (variation of B-site ionic radius $\langle r_B \rangle$) and also depends on the cooperative JT distortion of MnO_6 octahedra.

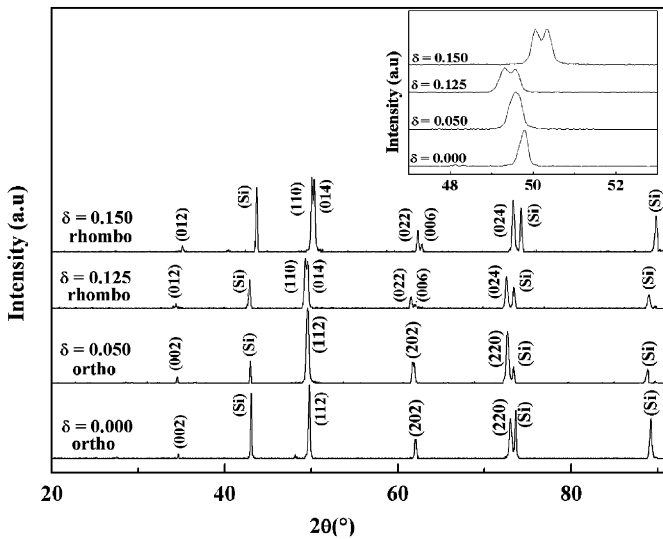


Fig. 1. X-ray diffraction patterns at room temperature of $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_{3-\delta}$ for $\delta = 0.000, 0.050, 0.125$ and 0.150 .

Table 1
Crystallographic data for $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_{3-\delta}$ compounds

δ	$\langle r_B \rangle (\text{\AA})$	$\text{Mn}^{3+} (\%)$	Structure	$a(\text{\AA})$	$b(\text{\AA})$	$c(\text{\AA})$	$V(\text{\AA}^3)$	Mn–O–Mn($^\circ$)
0.000	0.614	70	Ortho	5.472 ₂	5.462 ₉	7.728 ₃	57.757 ₅	144.499 ₈
0.050	0.626	80	Ortho	5.483 ₅	5.474 ₄	7.736 ₆	58.061 ₀	156.200 ₁
0.075	0.632	85	Ortho	5.485 ₂	5.472 ₆	7.745 ₂	58.124 ₅	165.000 ₀
0.100	0.638	90	Rhombo	5.491 ₂	5.491 ₂	13.371 ₂	58.195 ₈	168.799 ₉
0.125	0.644	95	Rhombo	5.496 ₉	5.496 ₉	13.365 ₉	58.292 ₅	173.799 ₉
0.150	0.650	100	Rhombo	5.505 ₁	5.505 ₁	13.375 ₆	58.509 ₁	174.188 ₃

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