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Effect of the oxygen deficiency on the physical properties of $La_{0.8}Na_{0.2}MnO_{3-\delta}$ oxides ($\delta=0$ and 0.05)

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ABSTRACT

This paper presents the effects of oxygen deficiency on the structural, magnetic and magnetocaloric properties of $La_{0.8}Na_{0.2}MnO_{3-\delta}$ where $\delta=0$ and 0.05. The Polycrystalline $La_{0.8}Na_{0.2}MnO_{3-\delta}$ samples were synthesized by a new method. The introduction of the oxygen deficiency in our samples leads to an increase of Mn^{3+} content according to the electronic formula $La^{3+}_{0.}Na^{+}_{0.2}Mn^{3+}_{0.6+2\delta}Mn^{4+}_{0.4-2\delta}O_{3-\delta}$.

The X-ray diffraction analysis shows a phase transition from a rhombohedral system with $R\bar{3}c$ space group for $\delta=0.00$ to an orthorhombic with *Pnma* space group for $\delta=0.05$. It also induces a great variation in the magnetic properties. The magnetization versus temperature study has shown that all samples exhibit a magnetic transition from ferromagnetic (FM) to paramagnetic (PM) phase with the increase in temperature. However, it can be clearly seen that the oxygen deficiency induces an increase in the magnetization and a decrease in the Curie temperature T_C. Besides, the magnetocaloric effect (MCE) as well as the Relative Cooling Power (RCP) has been estimated. As an important result, the values of MCE and RCP in our oxygen deficiency manganites are reported to be close to those found in gadolinium that is considered as magnetocaloric reference material.

1. Introduction

$Ln_{1-x}A_xMnO_3$ (Ln=Rare-earth cation, A=alkali-metal or alkaline earth cation) has attracted much attention due to the large magnetocaloric effect (MCE) in these compounds [1–3]. In fact, magnetic refrigeration has become a promising technology to replace the conventional gas-compression expansion technique [4,5]. For sub-room temperature magnetic refrigeration applications, gadolinium is the first material known to show a large MCE since it exhibits a maximum value of magnetic entropy change, ΔS_{Max}, of 5 J kg^{-1} K^{-1} at 294 K under magnetic applied field change of 2 T [6]. Otherwise, manganites are also interesting for application as potential candidates in magnetic refrigeration since not only do they have low cost but also they are easy to elaborate and possess tunable T_C and high chemical stability. Generally, in manganites, the large magnetic entropy change could be attributed to the variation of the double exchange interaction between Mn^{3+} and Mn^{4+} ions and the strong spin lattice coupling [7–9]. The classic methods used to change the Mn^{4+} content involves substituting La^{3+} by a divalent element or creating vacancies in the La, Mn, or O sites in $LaMnO_3$. These vacancies can be obtained by varying the synthesis conditions and subsequent annealing treatments [10–12].

A search for a new method of creating vacancies in the oxygen sites (oxygen content < 3) has been of interest thanks to the potential technological applications of these vacancies in solid oxide fuel combustible (SOFC), high-temperature electrolyzers, oxygen sensors, and catalysis. In order to clarify the oxygen deficiency effects on the structural, magnetic and magnetocaloric properties, $La_{0.8}Na_{0.2}MnO_{3-\delta}$ ($\delta=0$ and 0.05) has been prepared. In this system, the number of Mn^{3+} and Mn^{4+} ions systematically varies with δ. The developed electronic formula of the samples is $La^{3+}_{0.8}Na^{+}_{0.2}Mn^{3+}_{0.6+2\delta}Mn^{4+}_{0.4-2\delta}O_{3-\delta}$ Thus, the Mn^{3+} and Mn^{4+} concentrations are $(0.6+2\delta)$ and $(0.4-2\delta)$, respectively.

2. Experimental

The nonstoichiometric perovskite oxides $La_{0.8}Na_{0.2}MnO_{3-\delta}$ were prepared by creating vacancies in the oxygen sites in the $La_{0.8}Na_{0.2-x}MnO_3$ sample according to the equation that follows as

$$La_{0.8}Na_{0.2}MnO_3 + \frac{\delta}{2}Ti \rightarrow La_{0.8}Na_{0.2}MnO_{3-\delta} + \frac{\delta}{2}TiO_2 \quad (1)$$

Polycrystalline $La_{0.8}Na_{0.2}MnO_3$ sample was prepared by the standard ceramic technology. The detailed preparation procedure is the same as that in Ref. [13]. The sample was next placed in a quartz tube containing titanium in the stoichiometric proportion of Eq. (1). The tube was pumped, sealed, and annealed at 700 °C

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for 2 weeks. The X-ray powder diffraction (XRD) data were recorded at room temperature with Siemens D5000 diffractometer with CuKα ($\lambda = 1.5406$ Å) radiation. As for the magnetic measurements, they were performed in BS1 and BS2 magnetometer developed in Louis Néel Laboratory of Grenoble.

3. Results and discussion

3.1. X-ray diffraction analysis

The room temperature X-ray powder diffraction (XRD) measurements has shown clean single phase patterns for all samples.

Table 1
Results of Rietveld refinements, determined from XRD patterns measured at room temperature, for $La_{0.8}Na_{0.2}MnO_{3-\delta}$ ($\delta = 0$ and $\delta = 0.05$).

δ	**0**	**0.05**
Structure	Rhombohedral	Orthorhombic
Space group	$R\bar{3}C$	*Pnma*
a (Å)	5.4126	5.493
b (Å)	5.4126	5.438
c (Å)	13.1324	7.740
Unit cell volume (Å^3)	55.531	57.819
d_{Mn-O} **(Å)**	1.925	2.124
$\theta_{Mn-O-Mn}$ **(deg)**	164.587	174.010

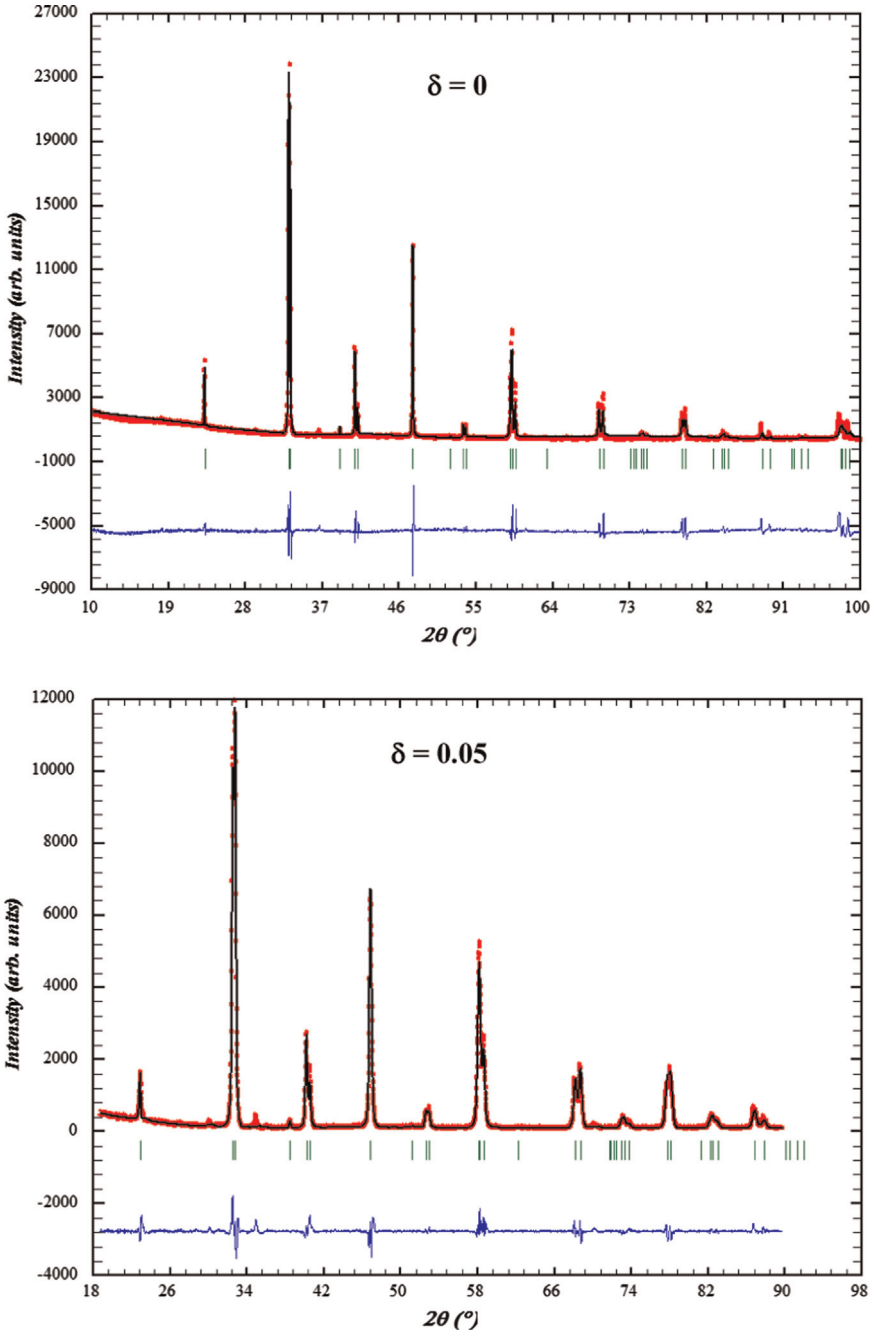

Fig. 1. Observed (open symbols) and calculated (solid lines) X-ray diffraction pattern for $La_{0.8}Na_{0.2}MnO_{3-\delta}$ ($\delta = 0.00$ and 0.05). Positions for the Bragg reflection are marked by vertical bars. Differences between the observed and the calculated intensities are shown at the bottom of the diagram.