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Study of physical properties of cobalt substituted $Pr_{0.7}Ca_{0.3}MnO_3$ ceramics

R. M'nassri[a,b], M. Khelifi[c], H. Rahmouni[c], A. Selmi[d,*], K. Khirouni[c], N. Chniba-Boudjada[e,f], A. Cheikhrouhou[d]

[a]Higher Institute of Applied Sciences and Technology of Kasserine, Kairouan University, B.P. 471, 1200 Kasserine, Tunisia
[b]Laboratoire de Physico-Chimie des Matériaux, Département de Physique, Faculté des Sciences de Monastir, Université de Monastir, 5019 Monastir, Tunisia
[c]Laboratoire de Physique des Matériaux et des Nanomatériaux appliquée à l'Environnement, Faculté des Sciences de Gabès cité Erriadh, Université de Gabès, 6079 Gabès, Tunisia
[d]Laboratory of Physics of Materials, Faculty of Sciences of Sfax, Sfax University, B.P. 1171, 3000 Sfax, Tunisie
[e]Faculté des Sciences de Gabès cité Erriadh, Université de Gabès, 6079 Gabès, Tunisia
[f]Institut NEEL, B.P. 166, 38042 Grenoble Cedex 09, France

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Abstract

An investigation on single phase semiconducting polycrystalline $Pr_{0.7}Ca_{0.3}MnO_3$ and $Pr_{0.7}Ca_{0.3}MnCo_{0.1}O_3$ crystallized in the orthorhombic system with Pnma space group is reported. We found that σ_{DC} increases when introducing Co for $T < 110$ K but for $T > 110$ K, it decreases. Also, the contribution of hopping process in conduction mechanism was in agreement with the Jonscher law and Mott theory. Capacitance was extensively dependent on temperature and frequency. A dielectric transition was observed at $T = 150$ K for the doped compound. The temperature dependence of dielectric permittivity is well described by Curie–Weiss law. The parameter of deviation from Curie–Weiss behavior to modified Curie–Weiss law is found to be $\Delta T_m = 30$ K. The substitution of Mn by Co was found to destroy the charge order state observed in the parent compound and to induce a ferromagnetic phase at low temperature. The cobalt-substituted sample exhibits a maximum value of magnetic entropy change $|\Delta S^{max}| = 3.2$ J kg^{-1} K^{-1} and a large relative cooling power with a maximum value of 301 J/kg under an applied field of 5 T. Technically, these large values make the prepared material very promising for magnetic refrigeration.

Keywords: C. Electrical properties; C. Magnetic properties; Manganites; Magnetocaloric effect; Master curves

1. Introduction

Manganite systems are particularly important because of their wide range of properties such as ferroelectricity, colossal magnetoresistance, superconductivity and applications in sensors, fuel cells, and computer memory systems, magnetoresistive transducers, infrared detectors and magnetic refrigerants [1–4]. The high sensitivity of such manganites systems to a variety of parameters including substitution site [5], doping element [6–10], oxygen stoichiometry [11], doping level [12], average cationic size [13], cationic disorder [14] grain boundary engineering [15], particle size [16,17] and the synthesis route [18–20] is a way for a large degree of tunability in magnetic and magnetocaloric behavior. These oxides exhibit a rich variety of physical properties including ferroelectricity, ferromagnetism and charge ordering (CO) related to the competing electron–lattice and electron–electron interactions [21–23]. Generally, the Mn ion exist in two different oxidation states such as Mn^{3+} and Mn^{4+}, which creates ferromagnetism and conduction in Pr-based manganites. This behavior is usually interpreted with the help of double exchange mechanism, where the magnetic coupling between Mn^{3+} and Mn^{4+} ions results from the motion of an electron between the two partially filled d-orbitals with strong on-site Hund's coupling [24]. Since, the strength of double-exchange interaction between Mn^{3+} and Mn^{4+} pairs and the lattice distortion have shown to play an important role in the properties of these materials [25]. In the present work, the structural, electrical, magnetic and magnetocaloric properties of $Pr_{0.7}Ca_{0.3}MnO_3$

*Corresponding author.
E-mail address: bohmids@gmail.com (A. Selmi).

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and $Pr_{0.7}Ca_{0.3}MnCo_{0.1}O_3$ have been investigated and the results are discussed.

2. Experimental details

$Pr_{0.7}Ca_{0.3}MnO_3$ and $Pr_{0.7}Ca_{0.3}MnCo_{0.1}O_3$ were prepared from high purity precursors: Pr_6O_{11}, $CaCO_3$, Co_3O_4 and Mn_2O_3 (Aldrich 99.9%; USA) by solid-state reaction at high temperature. The precursors were intimately mixed in an agate mortar. The obtained powders were then pressed into pellets and sintered at 800, 1000, 1100 and 1300 °C for 24 h for each cycle to ensure a better crystallization with intermediate regrinding and re-pelletizing [26]. Finally the samples were cooled from high temperature to room temperature following the cooling inertia of the furnace (~8 h) [27,28]. For both materials, phase purity and cell dimensions were determined by X-ray powder diffraction, recorded at room temperature on a PANalytical X'PERT Pro MPD diffractometer, using $\theta/2\theta$ Bragg–Brentano geometry with diffracted beam monochromatized Cu Kα radiation. The diffraction patterns were collected by steps of 0.017 over the angle range 10–80°. Structural analyses were carried out by the Rietveld method [29,30] using the FullProf software. Magnetic measurements were performed in BS2 magnetometer constructed at Néel Institute. Magnetocaloric results are deduced from the magnetization measurements versus magnetic applied field up to 5T at several temperatures. For electrical measurements, a thin silver film (20 nm thick) was deposited on the both side of the pellet through a circular mask of 6 mm of diameter. Then, we obtained a configuration of plate capacitor which is used to measure both the conductance and the capacitance. The sample is mounted in a cryostat to vary the temperature from 77 K to 300 K. Under vacuum and in dark, measurements are conducted with an Agilent 4294 analyzer using a signal amplitude of 20 mV.

3. Results and discussion

a. X-ray diffraction

The results of the XRD studies at room temperature of $Pr_{0.7}Ca_{0.3}MnO_3$ and $Pr_{0.7}Ca_{0.3}Mn_{0.9}Co_{0.1}O_3$ samples indicate that all prepared samples are single phase without any detectable impurity and crystallize in the orthorhombic system with the Pnma space group. The atoms (Pr, Ca) are located at 4c (x, 1/4, z), (Mn, Co) at 4b (1/2, 0, 0), O_1 at 4c (x, 1/4, z) and O_2 at (x, y, z). The Fig. 1 shows a typical Rietveld refinement for $Pr_{0.7}Ca_{0.3}Mn_{1-x}Co_xO_3$ registered at 300 K including the observed and calculated profiles as well as the difference profile. The quality of the refinement is evaluated through the goodness of the fit indicator χ^2 (1.21 for $x=0.0$ and 1.27 for $x=0.1$). The cell parameters for $Pr_{0.7}Ca_{0.3}MnO_3$ are found to be $a=5.459(8)$ Å, $b=7.674(1)$ Å, $c=5.430(3)$ Å and the unit cell volume $V=227.52$ Å^3. For $Pr_{0.7}Ca_{0.3}Mn_{0.9}Co_{0.1}O_3$, there are found to be $a=5.430(6)$ Å, $b=7.670(5)$ Å, $c=5.448(4)$ Å and $V=226.96$ Å^3.

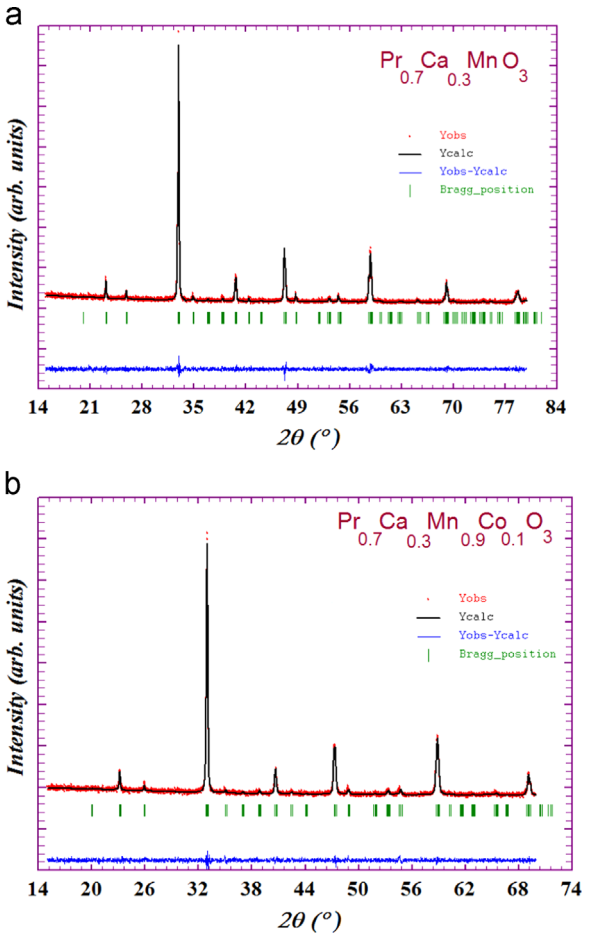

Fig. 1. X-ray powder diffraction patterns and refinement at room temperature for: (a) $Pr_{0.7}Ca_{0.3}MnO_3$ and (b) $Pr_{0.7}Ca_{0.3}Mn_{0.9}Co_{0.1}O_3$.

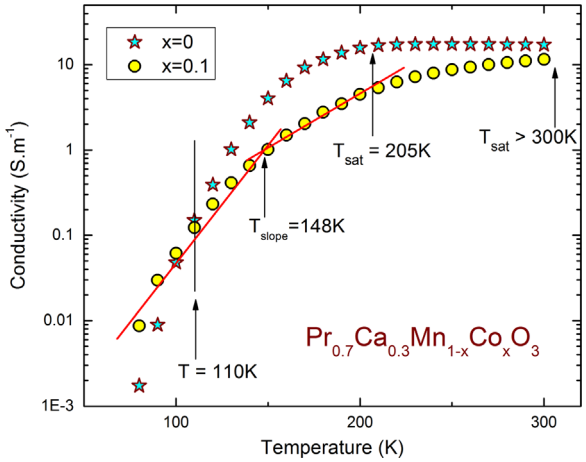

Fig. 2. Temperature dependence of DC conductivity of $Pr_{0.7}Ca_{0.3}MnO_3$ and $Pr_{0.7}Ca_{0.3}Mn_{0.9}Co_{0.1}O_3$ samples.

b. DC conductivity study

The variation of dc-conductivity as a function of temperature is shown in Fig. 2. The investigated samples show a semiconductor behavior. When increasing temperature, it is observed that dc-conductivity increases. For the undoped compound, a saturation region is observed. Such region starts