Physica B 403 (2008) 4012–4019

Contents lists available at ScienceDirect

Physica B

journal homepage: www.elsevier.com/locate/physb

Effects of sodium doping on physical properties of $La_{0.75}Sr_{0.25-x}Na_xCoO_3$ ($0 \leqslant x \leqslant 0.2$) cobaltites

M. Koubaa [a], W. Cheikhrouhou-Koubaa [a], A. Cheikhrouhou [a,b,*], L. Ranno [b]

[a] Laboratoire de Physique des Matériaux, Faculté des Sciences de Sfax, B.P.802, Sfax, Tunisia
[b] Institut NEEL, CNRS, B.P.166, 38042 Grenoble cedex9, France

ARTICLE INFO

Article history:
Received 1 February 2008
Received in revised form
29 July 2008
Accepted 30 July 2008

Keywords:
Cobaltite
Magnetic properties
Magnetocaloric effect
Spin state

ABSTRACT

The effects of Na doping on the crystallographic, magnetic, electrical and magnetocaloric properties of $La_{0.75}Sr_{0.25-x}Na_xCoO_3$ ($0 \leqslant x \leqslant 0.2$) samples, elaborated using the solid-state reaction method at high temperature, have been investigated. X-ray powder diffraction studies reveal that all our synthesized samples crystallize in the rhombohedral structure ($R\bar{3}c$ space group). Na substitution leads to an enhancement of the Co–O bond length and a reduction in the Co–O–Co bond angle and consequently to a weakening of the double exchange interaction between Co^{3+} and Co^{4+} ions. The zero field cooled (ZFC) and field cooled (FC) magnetization curves at 50 mT show thermomagnetic irreversibility. At low temperatures, with increasing Na amount, the samples change from ferromagnetic-like behavior ($x = 0$, 0.05 and 0.1) to spin-glass one ($x = 0.15$ and 0.2). The ferromagnetic–paramagnetic transition temperature decreases with increasing Na amount from 235 to 200 K ($x = 0.1$). The critical exponent value, associated to the spontaneous magnetization, increases with increasing Na amount from 0.37 for $x = 0$ to 0.57 for $x = 0.1$. The temperature dependence of the electrical resistivity reveals three different regimes as a function of Na content: (i) for $x = 0$, a metallic behavior is observed in the whole temperature range, (ii) for $x = 0.05$, a metal-semiconducting transition is observed around 80 K and (iii) for $x \geqslant 0.1$, we observe a semiconducting behavior in the whole temperature range. The parent compound ($x = 0$) exhibits a maximum entropy change $|\Delta S_M^{MAX}|$ of 0.84 J kg^{-1} K^{-1} at 220 K in a magnetic applied field of 2 T. $|\Delta S_M^{MAX}|$ decreases to 0.47 J kg^{-1} K^{-1} at 185 K for $x = 0.1$ in the same field magnitude. Well above T_C, $|\Delta S_M^{MAX}|$ shows a linear dependence as a function of H^2 indicating the existence of spin fluctuations inside ferromagnetic clusters.

1. Introduction

Cobaltites with general formula $Ln_{1-x}M_xCoO_3$ (Ln = La, Pr, etc. and M = Sr, Ca, etc.) have received recently considerable interest. In fact these materials exhibit rich variety of phenomena such as colossal magnetoresistance effect, phase separation in addition to the existence of various spin state of Co^{3+} and Co^{4+} ions [1–5]. Besides fundamental understanding of unusual magnetic properties, studies have been also motivated by potential applications of these oxides (magnetoresistance devices, cathode material for solid oxide fuel cells (SOFC), etc.) [6–10]. In $LaCoO_3$ compound, the magnetic susceptibility curve versus temperature shows on warming two broad transitions occurring, respectively, around T_{S1} and T_{S2} ($20\,K \leqslant T_{S_1} \leqslant 100\,K$ and $400\,K \leqslant T_{S_2} \leqslant 700\,K$) [11]. It has been suggested that, the first one (at T_{S_1}) is due to spin state transition of Co^{3+} ions from non-magnetic low-spin state (LS, $S = 0$, t_{2g}^6) to paramagnetic intermediate spin state (IS, $S = 1$, $t_{2g}^5 e_g^1$), while the second one (at T_{S_2}) is due to the population of Co^{3+} high-spin state (HS, $S = 2$, $t_{2g}^4 e_g^2$) [12]. This behavior has been understood in terms of the comparable energy magnitude of the crystal field splitting and Hund's rule coupling [13]. The substitution of La^{3+} by Sr^{2+} results in conversion of an appropriate amount of Co^{3+} to Co^{4+}. $La_{1-x}Sr_xCoO_3$ compounds in the range $0 \leqslant x \leqslant 0.5$ exhibit rich phase diagram: spin glass ($x \leqslant 0.18$), cluster glass ($0.18 < x \leqslant 0.25$) and ferromagnetic phase ($0.25 < x \leqslant 0.5$) [14]. It is well known that the origin of the spin/cluster glass state may be explained by the competition between ferromagnetic double exchange interaction (Co^{3+}–O–Co^{4+}) within the cluster and antiferromagnetic super-exchange interactions (Co^{3+}–O–Co^{3+} and Co^{4+}–O–Co^{4+}) between clusters [15–17]. For $x = 0.18$, the isolated ferromagnetic metallic cluster size embedded in a non-ferromagnetic matrix is about 30 Å at low temperature [18]. As x increases in $La_{1-x}Sr_xCoO_3$ samples ($x \geqslant 0.2$), the unusual magnetic properties (thermomagnetic irreversibility) have been explained by the coalescence of short-range-ordered ferromagnetic clusters [19]. Besides doping

* Corresponding author at: Laboratoire de Physique des Matériaux, Faculté des Sciences de Sfax, B.P.1171, 3000 Sfax, Tunisia. Tel./fax: +216 74 676607.
E-mail address: abdcheikhrouhou@yahoo.fr (A. Cheikhrouhou).

0921-4526/$ - see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.physb.2008.07.044

level (Co^{4+} amount), properties of cobaltites can be considerably controlled by average ionic radius $\langle r_A \rangle$ of the A-cation site. In (La,Sr)CoO_3 cobaltites, when La ions are partially substituted by Gd ions with smaller ionic radius, magnetic properties show a transition from cluster glass to spin-glass state [20]. The results of magnetic and transport properties reported on $(La_{1-x}Ln_x)_{0.5}Sr_{0.5}CoO_3$ (Ln = Pr, Nd) show that with decreasing $\langle r_A \rangle$, ferromagnetic transition temperature shifts to lower values and both values of resistivity and magnetoresistance ratio increase [21]. These authors explained their results by assuming that the spin disorder scattering inside the magnetic domains increases. Studies of Kundu et al. [22] on $La_{0.7-x}R_xCa_{0.3}CoO_3$ (R = Pr, Nd, Gd, Dy) with fixed carrier concentration reveal that the decrease in $\langle r_A \rangle$ leads to a weakening of the ferromagnetism due to magnetic-phase separation between hole-rich large ferromagnetic regions and hole-poor low-spin regions occurring in these samples. Our previous studies on the lanthanum and strontium vacancies effects of $La_{0.7}Sr_{0.3}CoO_3$ cobaltites have shown that with increasing vacancy content, magnetization exhibits a different behavior depending on the vacancy type [23,24]. Lanthanum-deficient samples showed that the presence of vacancies leads to a gradual change from cluster glass state to ferromagnetic one. The Curie temperature T_C is found to increase with deficiency amount. However, strontium-deficient samples undergo a gradual change from cluster glass state to spin-glass one. The divalent alkaline-earth-metal doping in lanthanum cobaltites have been widely studied. However, only few studies on the monovalent metal-doping effects have been reported. Moreover, in perovskite manganites which undergo physical properties similar to that observed in cobaltites as a function of hole doping, monovalent substitution is expected to introduce large potential fluctuations leading to large magnetoresistive and magnetocaloric effects [25,26]. In this work, we report the effect of the Na doping on the structural, magnetic, electrical and magnetocaloric properties of $La_{0.75}Sr_{0.205-x}Na_xCoO_3$ samples.

2. Experimental techniques

Polycrystalline $La_{0.75}Sr_{0.25-x}Na_xCoO_3$ ($0 \leqslant x \leqslant 0.2$) samples were synthesized using the standard solid-state reaction method at high temperature, by mixing La_2O_3, $SrCO_3$, Na_2CO_3 and Co_3O_4 up to 99.9% purity in the desired proportions. The starting materials were intimately mixed in an agate mortar and then heated in air up to 1000 °C for 60 h. The obtained powders were then pressed into pellets (of about 1 mm thickness and 13 mm diameter) and sintered at 1150 °C in air for 60 h with intermediate regrinding and repelling. Finally, these pellets were rapidly quenched to room temperature in air in order to freeze the structure at the annealed temperature. Phase purity, homogeneity and cell dimensions were determined by powder X-ray diffraction (XRD) at room temperature. Structural refinement was carried out using the standard Rietveld technique [27,28]. The amount of Co^{4+} ions has been quantitatively checked by iodometric titration [29]. Magnetization measurements versus temperature in the range 20–300 K were performed using a vibrating sample magnetometer. In the field cooled (FC) mode, magnetization measurements were performed while cooling the sample to 20 K in a magnetic applied field of 50 mT. In the zero field cooled (ZFC) mode, magnetization measurements were performed by warming the sample under the same magnetic applied field after cooling to 20 K in zero magnetic field. Isothermal magnetization curves $M(H)$ were carried out up to 8 T. Resistivity measurements versus temperature were performed by the standard four-probe method on sintered bars.

3. Results and discussion

XRD patterns at room temperature of all our synthesized samples have been indexed in the rhombohedral lattice with $R\bar{3}c$ space group. Structural parameters are refined by Rietveld's profile-fitting method. The process of refinement is started with scale and background parameters followed by the unit cell parameters. Then, the peak asymmetry and preferred orientation corrections are applied. Finally, positional parameters and individual isotropic parameters are refined. The atomic occupations were set in terms of formula and not refined in this work. It is relevant that all samples contain a small amount of impurity phase, which can be identified as CoO. The CoO phase has been included in the refinement as secondary phase. The residual amount of CoO, as obtained by Rietveld analysis, increases with increasing Na amount from 3% for $x = 0$ to 8% for $x = 0.2$. The CoO phase has also been observed in other cobaltites synthesized by solid-state reaction at 1150 °C [30,31]. Typical experimental and refined XRD patterns for two representative samples ($x = 0$ and 0.05) are shown in Fig. 1. Detailed results of structural parameters deduced from Rietveld analysis of XRD data are summarized in Table 1. The rhombohedral structure of our polycrystalline samples is derived from the distortion of the ideal cubic perovskite structure. In fact, according to the ionic model of Goldschmidt, a tolerance factor $t = \langle r_A \rangle + r_O/\sqrt{2}(R_{Co} + r_O)$ is around 1 for ideal cubic perovskite while for t value slightly less than 1, the CoO_6 octahedra are tilted around the [1 1 1] axis leading to rhombohedral distortion. For polycrystalline sample with $R\bar{3}c$ space group, the allowed reflexions ($h\,k\,l$) correspond to the condition $-h+k+l = 3n$ as observed in our diffractograms. The lattice parameter $a(b)$ remains almost unchanged for all samples; however, the lattice parameter c decreases by 0.6% from 13.194 Å ($x = 0$) to 13.117 Å ($x = 0.2$). The unit cell volume decreases also with increasing Na content (Fig. 2a). We can observe that the volume evolution as a function of Na content follows a linear decrease with two different slopes corresponding to a rate of $dV/dx \sim 5$ Å^3 for x below 0.1 and $dV/dx \sim 12$ Å^3 for x above 0.1. As Na doping induces an increase of Co^{4+} content with average ionic radius less than Co^{3+} (in the octahedral oxygen coordination $r(Co^{3+})IS = 0.56$ Å, $r(Co^{3+})HS = 0.61$ Å and $r(Co^{4+})HS = 0.53$ Å [32]), the reduction of the unit cell volume with increasing Na amount can be explained by the increase of the Co^{4+} content. The decrease of the unit cell volume may be also explained by a smaller average ionic radius in the A-site induced by Na substitution. It can be seen from Fig. 2b that with increasing Na amount, Co–O–Co bond angle decreases from 166.44° for $x = 0$ to 161.27° for $x = 0.2$ whereas Co–O bond length displays inverse correlation to variation in Co–O–Co bond angle. This result implies that the ferromagnetic exchange interaction between Co ions is reduced due to a decrease in the charge transfer integral and in the band width of the Co 3d and O 2p bands. Luo et al. [33] have studied the effect of rare-earth doping on the properties of $La_{0.75-x}A_xSr_{0.25}CoO_3$ (A = La, Nd, Gd, Ho, Y) cobaltites. They have shown that when $\langle r_A \rangle$ increases, Co–O–Co bond angle decreases from 167.72° (A = La) to 166.02° (A = Y) while Co–O bond length remains almost constant for all substitutions. This difference may be due to the difference in elaborating technique (annealing temperature).

Fig. 3 displays the temperature dependence of the FC magnetization in a magnetic applied field of 50 mT for all our samples. For $x \leqslant 0.1$, a paramagnetic to ferromagnetic transition is observed. Curie temperature T_C (determined from the inflection point of magnetization curves) is found to be 235, 229 and 200 K for $x = 0$, 0.05 and 0.1, respectively. While for $x > 0.1$ magnetization increases linearly with decreasing temperature at about 240 K indicating the onset of ferromagnetic ordering within the clusters.