Journal of Alloys and Compounds 681 (2016) 547–554

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

Effect of cobalt on structural, magnetic and magnetocaloric properties of $La_{0.8}Ba_{0.1}Ca_{0.1}Mn_{1-x}Co_xO_3$ (x = 0.00, 0.05 and 0.10) manganites

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ARTICLE INFO

Article history:
Received 14 January 2016
Received in revised form
25 March 2016
Accepted 15 April 2016
Available online 19 April 2016

Keywords:
Structural
Magnetization
Magnetocaloric effect
Magnetic entropy change
Relative cooling power

ABSTRACT

We have studied the effect of Co substitution on the structural, magnetic and magnetocaloric (MCE) properties of $La_{0.8}Ba_{0.1}Ca_{0.1}Mn_{1-x}Co_xO_3$ compounds with x = 0.00, 0.05 and 0.10. All samples were synthesized using polymerization complex sol-gel method. X-ray diffraction (XRD) studies show that all compositions crystallize in the rhombohedral structure with the $R\overline{3}c$ space group. Rietveld analysis indicates that each (Mn, Co)O_6 octahedron has a little distortion and that the $\theta_{(Mn,\ Co)-O-(Mn,\ Co)}$ bond angles decreases with increasing Co content. The zero field cooled (ZFC) and field cooled (FC) magnetizations reveal that all samples undergo a paramagnetic-ferromagnetic (PM-FM) phase transition and a large deviation is usually observed between ZFC and FC curves which is due to the presence of competing FM and antiferromagnetic (AFM) interactions leading to a glassy behavior. The Curie temperature (T_C) is found to decrease from 282 K for x = 0.00–214 K for x = 0.10. Arrot's plots reveal a second order nature of magnetic transition for all samples, which is also confirmed by landau's theory and universal curves.

1. Introduction

Perovskite manganites with the formula $(Tr^{3+}_{1-x}A^{2+}_x)(Mn^{3+}_{1-x}Mn^{4+}_x)O^{2-}_3$, where ($Tr^{3+}$ = La^{3+}, Sm^{3+}, Pr^{3+}, Nd^{3+}, etc., and A^{2+} = Ca^{2+}, Ba^{2+}, Sr^{2+}, etc.) have been the subject of much research. This thanks to their extraordinary magnetic and electronic properties, as well as to being very promising for future technological applications [1–6]. In addition, these materials have many advantages, such as their low cost production cost, convenient preparation high refrigeration efficiency, small volume requirement and chemical stability. Moreover, they are environment-friendly, non toxic and do not causes noise pollution. This makes them attractive to further research in relation widely-used refrigeration technology based on gas compression. A relationship between electrical transport and magnetism in these materials has been explained by many theories, such as double-exchange (DE) interaction [7], Jahn-Teller effect [8] and phase separation [9]. The parent compound, $LaMnO_3$, where Mn ions in the +3 valence, is an AFM insulator characterized by a super-exchange (SE) coupling between Mn^{3+} sites facilitated by a e_g electron. The introduction of a divalent or monovalent ion instead of La into perovskites results in a mixed valence state of Mn^{3+} and Mn^{4+}, respectively with the electronic configuration $(3d^4, t^3_{2g}\uparrow e^1_g\uparrow, S = 2)$ and $(3d^3, t^3_{2g}\uparrow e^0_g, S = 3/2)$ out of which the e_g electrons can be delocalized. This shows that the substitution at the La-sites does ultimately affect the Mn-sites ions the $La_{1-x}A_xMnO_3$ perovskite structure. This gives rise to a DE [10] transfer of spin-polarized electrons from Mn^{3+} to Mn^{4+}. In manganites, it is possible to dope at both T_r and Mn-sites, where T_r-sites doping is known to control the Mn^{3+}/Mn^{4+} ratio in the material. Compared with Tr-site doping, Mn-site doping is more important because it not only modifies the Mn^{3+}–O–Mn^{4+} network but also brings about the doped transition metal ions. It is believed that the study of doping effects at the Mn-site by other elements with different valences (Fe, Co, Cr, Ni, etc…), as electronic configuration and ionic radii, is very important because of the curial role of Mn ions in colossal magnetoresistance materials. Concerning the influence of Co doping in Mn-site on the structural, magnetic and MCE properties of doped perovskites $Tr_{1-x}A_xMnO_3$, many experimental

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http://dx.doi.org/10.1016/j.jallcom.2016.04.143
0925-8388/

results in manganites doped with Co for Mn at different concentrations show that Co substitution for Mn decreases the magnetic ordering of the unsubstituted manganites and makes the DE interaction of Mn^{3+}–O–Mn^{4+} short range. So, even a small amount of Co can be destroy the long-range FM order of the unsubstituted compound and results in a cluster (CG) or spin glass (SG) state formation [11–13]. In the perovskite manganites, the introduction of other transition metal elements, which exhibit the dissimilar electronic configuration to Mn-site, shall lead to dramatic effects associated with the electronic configuration mismatch between Mn and the other substituted magnetic ions. Therefore, it is interesting to study the study the effect of substituting the 3d magnetic element for Mn-site. As a contribution to the investigation of manganite materials, we report here the study of the effect of Co doping in the $La_{0.8}Ba_{0.1}Ca_{0.1}MnO_3$ polycrystalline samples, on the structural and magnetic properties and MCE effect.

2. Experimental

Polycrystalline samples $La_{0.8}Ba_{0.1}Ca_{0.1}Mn_{1-x}Co_xO_3$ (x = 0.00, 0.05 and 0.10) were prepared by polymerization complex sol-gel method. The details of the preparation procedure were reported in Ref. [14]. Phase purity, homogeneity, and cell dimensions are determined by powder XRD. The phase analysis was carried out using FULLPROF program based on Rietveld method. The microstructure was observed by scanning electron microscope (SEM) using a Philips XL30 and semi-quantitative analysis was performed at 20 kV accelerating voltage using energy dispersive X-ray analyses (EDX). ZFC and FC magnetization measurements vs. temperature (T) in an applied magnetic field of 0.05 T and magnetization (M) vs. magnetic field (μ_0H) (0-5T) were measured using a BS2 magnetometer developed in Louis Neel Laboratory of Grenoble.

3. Results and discussion

3.1. Structural properties

The powder XRD patterns for the polycrystalline $La_{0.8}Ba_{0.1}Ca_{0.1}Mn_{1-x}Co_xO_3$ (x = 0.00, 0.05 and 0.10) collected at room temperature are shown in Fig. 1. XRD data were analyzed using Rietveld refinement in FULLPROF program [15]. From Fig. 1, we can note that all samples have a single phase without any detectable secondary phase, within the sensitivity limits of the experiment. Moreover, no structural transition occurred in the $La_{0.8}Ba_{0.1}Ca_{0.1}Mn_{1-x}Co_xO_3$ (x = 0.00, 0.05 and 0.10) samples. Fig. 2 exemplifies the Rietveld refinement XRD profile for $La_{0.8}Ba_{0.1}Ca_{0.1}Mn_{0.9}Co_{0.1}O_3$ sample, with a good agreement between observed and calculated profiles, due to the excellent goodness of χ^2. The analyzed data showed that all samples crystallize in the rhombohedral structure with $R\overline{3}c$ (Z = 6) space group, in which La/Ba/Ca atoms are 6a at (0, 0, 1/4) position, Mn/Co at 6b (0, 0, 0) and O at 18e (x, 0, 1/4) position. The unit cell and some fitting parameters of all samples are given in Table 1. To describe the ionic match between A and B site ions in the perovskite structure compound ABO_3, a geometrical quantity, tolerance factor t_G is usually introduced. t_G is defined as:$t_G = \left(\frac{\langle r_A\rangle+\langle r_O\rangle}{\sqrt{2}(\langle r_B\rangle+\langle r_O\rangle)}\right)$ [16], $\langle r_i\rangle$ (i = A, B or O) represents the average ionic size of each element. Oxide based manganite compounds have a perovskite structure if their tolerance factor lies in the limits of $0.89<t_G < 1.02$ [17] and in an ideal case the value must be equal to unity. The values of t_G were estimated and listed in Table 1 which is within the range of stable perovskite structure. For the current investigated samples, the average ionic radius of A-site is fixed. Therefore, a decrease in the lattice from x = 0.00 to 0.10 is caused by the partial replacement of Mn (r_{Mn3+} = 0.65 Å) by a smaller Co^{3+} ions (r_{Co3+} = 0.61 Å) [18]. The departure from the average radius of Mn ions at the dopant site subjects the neighboring Mn–O bonds to a centric pull. Only the smaller ion at the dopant site can compress some Mn–O–Mn bonds and result in decreasing the average Mn–O–Mn bond angle. This hypothesis was confirmed by the determination, from the Rietveld refinement, of (Mn/Co)–O distance calculated from the structural parameters (see Table 1). The order of evolution of these results is in agreement with Those That are found in the references [19–23]. It has been reported that the deformation of the (Mn/Co)O_6 octahedron may be required to account for lattice distortion of the perovskite structures. The crystal structure of $La_{0.8}Ba_{0.1}Ca_{0.1}Mn_{0.9}Co_{0.1}O_3$ compound was drawn using 'Diamond' program (shown in inset of Fig. 2).

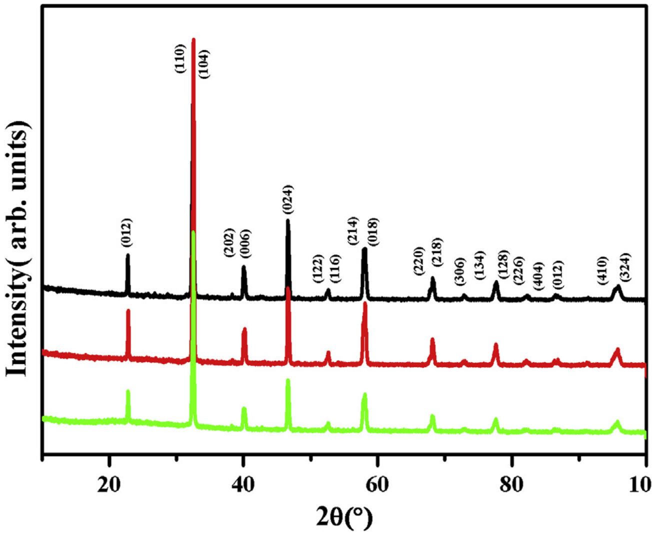

Fig. 1. Powder XRD pattern for the $La_{0.8}Ba_{0.1}Ca_{0.1}Mn_{1-x}Co_xO_3$ (x = 0.00, 0.05 and 0.10) compounds at room temperature. All peaks of the manganite phase are indexed in the rhombohedra $R\overline{3}c$ symmetry.

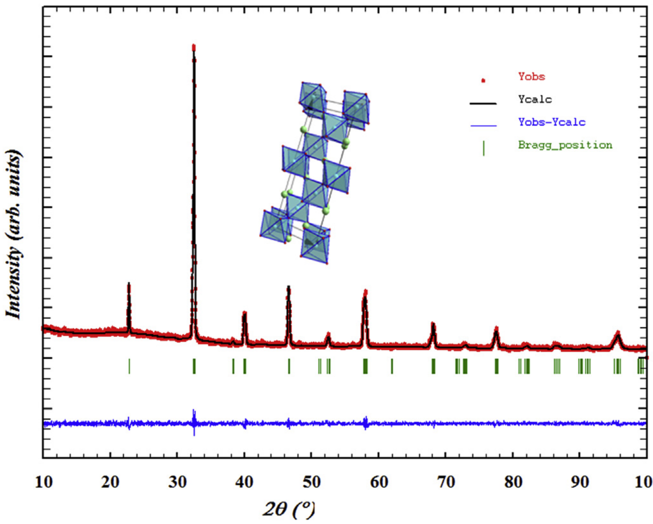

Fig. 2. The observed (symbol) and calculated (solid line XRD patterns obtained by Rietveld refinement for x = 0.10 specimen are shown in the right upper inset. The vertical lines show the Bragg peak positions and the difference between the data and the calculation is shown at the bottom. Crystal structure of $La_{0.8}Ba_{0.1}Ca_{0.1}Mn_{0.9}Co_{0.1}O_3$ sample.