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Magnetocaloric and magnetoresistance properties of $La_{2/3}Sr_{1/3}Mn_{1-x}Co_xO_3$ compounds

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Abstract

Structural, magnetic, magnetoresistance and magnetocaloric studies on $La_{2/3}Sr_{1/3}Mn_{1-x}Co_xO_3$ compounds were reported. The samples were prepared by the conventional ceramic method. X-ray analysis showed the presence of one phase only, in all studied samples. From electrical resistance measurements it was found that the samples show large negative magnetoresistance behavior. The magnetic measurements were performed in a large temperature range, 4.2–750 K and external magnetic fields up to 5 T. The adiabatic magnetic entropy changes, $|\Delta S|$, were determined from magnetization data. Large magnetocaloric effect (MCE) has been obtained in all studied samples.

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Keywords: Magnetic oxides; Colossal magnetoresistance; Magnetocaloric effect

1. Introduction

Magnetic materials showing a large magnetocaloric effect (MCE) have attracted considerable attention for their potential application in magnetic refrigeration technology [1–3]. MCE is an isothermal magnetic entropy change or an adiabatic temperature change of a magnetic material upon application of a magnetic field. The compounds that undergo temperature-driven paramagnetic to ferromagnetic transitions show relatively large "negative" MCE, in which the isothermal magnetic entropy change is negative [4]. Refrigeration in the temperature range 250–300 K is of particular interest due to the potential impact on energy savings and environmental concerns.

The interplay between structure, magnetic and transport properties in perovskite-type manganites was the aim of many recent papers. The substitution of the trivalent element by a divalent one produces an inhomogeneous distribution of mixed valence Mn^{4+}/Mn^{3+} ions to maintain charge neutrality. These systems exhibit many significant properties like charge and orbital ordering, metal–insulator transition, ferromagnetic–paramagnetic phase change, magnetoresistance, MCE, spin-glass behavior depending on the charge density, temperature and atomic structure [5–7]. Colossal magnetoresistance phenomena were observed in the perovskite-type hole-doped manganites in which the double-exchange ferromagnetic metal phase and the charge–orbital ordered antiferromagnetic phase compete with each other. The chemical randomness or the impurity doping may cause major modifications in the electronic phase diagram as well as in the magnetoelectronic properties. At present, the perovskite manganites are the most representative materials system that can show versatile unconventional electronic-lattice structural changes or insulator–metal transitions upon stimulation by external stimuli, like magnetic field, irradiation with light, X-rays or electron-beams.

Many of the manganite compounds, $R_{1-x}M_xMnO_3$, where R = rare-earth metal and M = Ca, Sr or Ba, exhibit large or unusual MCE values [8]. On the other hand, these materials display considerably small magnetic hysteresis and their Curie temperature can be tuned easily. The former is beneficial for the magnetic cooling efficiency and

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the latter is advantageous to the wide working temperature ranges.

$LaCoO_3$ is a diamagnetic insulator at low temperatures with a low spin state (LS) of Co^{3+} ($S=0$). The substitution of Sr^{2+} for La^{3+} in this compound converts a number of Co^{3+} to Co^{4+} ions. Co^{3+} ions can be in LS ($S=0$), intermediate spin (IS, $S=1$) or high spin (HS, $S=2$), while Co^{4+} can be in LS ($S=\frac{1}{2}$), IS ($S=\frac{3}{2}$) or HS ($S=\frac{5}{2}$). In this paper we analyze the influence of Co substitution at Mn sites on the physical properties and the MCE in $La_{2/3}Sr_{1/3}Mn_{1-x}Co_xO_3$ compounds.

2. Experimental

Polycrystalline samples with nominal composition $La_{2/3}Sr_{1/3}Mn_{1-x}Co_xO_3$ ($x=0.5$, 0.6, 0.7 0.8, 1) were prepared by standard ceramic reaction at high temperatures. The mixtures of the respective oxides were calcinated at 1200 °C and then were pressed and sintered in air at 1300 °C for 24 h. The powder X-ray diffraction patterns were recorded by using a Bruker D8 Advance AXS diffractometer with Cu Kα radiation. An Oxford Instruments MagLab System 2000 was used for magnetization measurements. The samples were studied in magnetic fields up to 5 T in the temperature ranges 4.2–750 K. The resistivities were measured in a cryogen-free cryostat CFM-7T (Cryogenic Ltd.) by the four-probe technique. The magnetic entropy changes were determined from magnetization isotherms, between zero field and a maximum field (H_0) using the thermodynamic relation

$$\Delta S_m(T,H_0) = S_m(T,H_0) - S_m(T,0) = \frac{1}{\Delta T}\int_0^{H_0}[M(T+\Delta T,H) - M(T,H)]\,dH \quad (1)$$

where ΔT is the temperature increment between measured magnetization isotherms ($\Delta T = 5$ K for our data). The magnetic cooling efficiency was evaluated by considering the magnitude of the magnetic entropy change, ΔS_m and its full-width at half-maximum (δT_{FWHM}). The product of the ΔS_m maximum and the ($\delta T_{FWHM} = T_2 - T_1$):

$$RCP(S) = -\Delta S_m(T,H) \times \delta T_{FWHM} \quad (2)$$

is the so-called relative cooling power (RCP) based on the magnetic entropy change.

3. Results and discussions

The X-ray diffraction patterns of $La_{2/3}Sr_{1/3}Mn_{1-x}Co_xO_3$ showed that the compounds are single phases, within the limit of experimental errors. All the compounds crystallize in a rhombohedral structure. The lattice parameters decrease slightly when the Co content increases. The monotonic decrease of the unit cell volume, with increasing cobalt content, indicate a random distribution of the Mn and Co ions in the lattice, i.e. not long-range Co/Mn order [9].

Some magnetization isotherms for the compounds with $x=1$ and 0.6 are plotted in Fig. 1. One can see that the saturation is not attended even in 5 T external magnetic field. Similar behaviors were obtained in all cases. In addition, low magnetic hysteretic behavior was found in $M(H)$ curves at low temperatures. The Curie temperatures decrease from 212 K at $x=1$ to 147 K at $x=0.5$. In the higher temperature region, 300–750 K, the reciprocal static magnetic susceptibility, $1/\chi$, has almost a linear behavior. The paramagnetic Curie temperatures for the samples having high Co contents are negative, antiferromagnetic interactions becoming dominant. When $x=1$ the Co^{3+} ions were found in all the three states LS, IS and HS.

The electrical resistivity measurements indicated semiconductor behavior for all the studied samples on the whole temperature range. Negative magnetoresistance $MR = [\rho(H)-\rho(0)]/\rho(0)$ has been found for all the

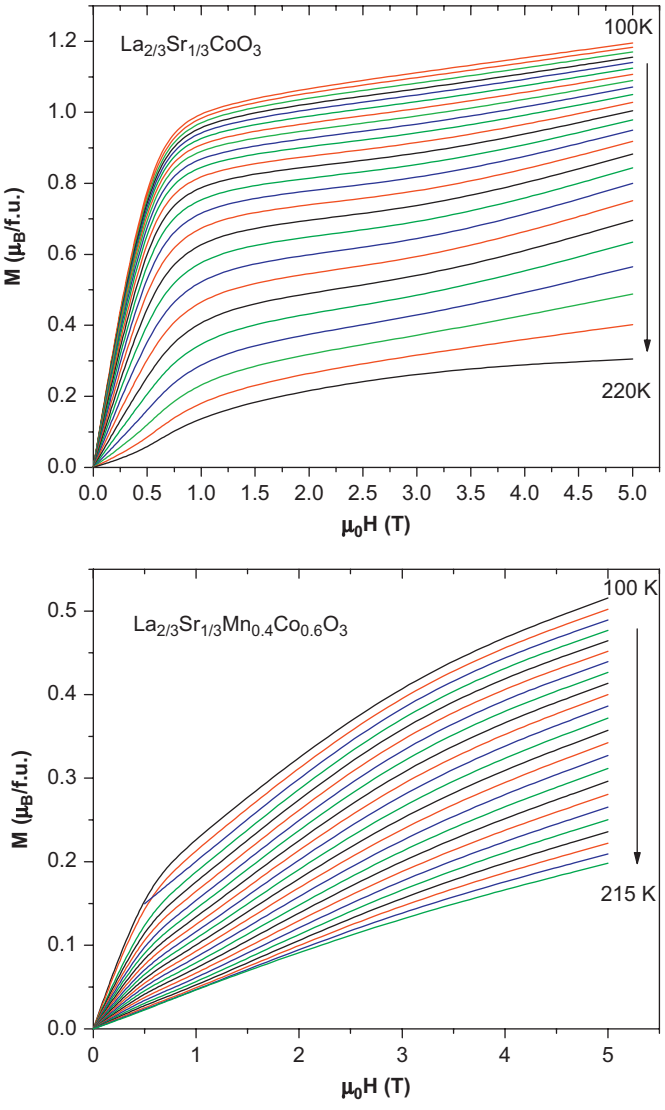

Fig. 1. Magnetization isotherms for the compounds with $x=1$ and 0.6.