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Electrical and magnetic properties of $La_{0.835}Na_{0.165}Mn_{0.9}RE_{0.1}O_3$ (RE=Mg, Cr, Ti) films prepared by chemical solution deposition method

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Abstract

$La_{0.835}Na_{0.165}Mn_{0.9}RE_{0.1}O_3$ (RE=Mg, Cr, Ti) films were prepared by chemical solution deposition method on $LaAlO_3$ (100) substrates. All the as-grown thin films are highly (h00) oriented with pseudocubic structure. There is a transition from the paramagnetic to ferromagnetic state in all the samples, but the substitution of Mn^{3+} ions by Mg^{2+} ions appears spin-glass cluster in the low temperature. Additionally, the sample $La_{0.835}Na_{0.165}Mn_{0.9}Mg_{0.1}O_3$ has the lowest Curie temperature and the metal-insulating transition temperature, and the resistivity is the highest. The resistivity curve exhibits insulating behavior in the temperature range of 100–390 K. The results are discussed in terms of the blocking of the percolative channel and the electric and magnetic disorder because of the substitution of a nonmagnetic ion.

Keywords: Chemical solution deposition; Perovskites; Colossal magnetoresistance; X-ray diffraction; Magnetic properties

1. Introduction

Rare-earth manganese oxides of the form $Ln_{1-x}A_xMnO_3$ (Ln=rare-earth element, A=alkaline-earth elements) have attracted considerable scientific and technological interest due to their rich physical properties and potential applications [1–5]. It has been shown that the spin, charge, and lattice are strongly coupled in these compounds. Zener has proposed the double exchange model to explain the concurrent occurrence of ferromagnetism and metallic transport [6–8], but more and more reports have revealed the lattice distortion could play an important role through strong electron-lattice coupling, which arises from the Jahn–Teller (JT) distortion around Mn^{3+} ions [9,10].

An important way to study the crucial role of Mn^{3+}–O–Mn^{4+} networks is to dope at the Mn site by other ions. Much work have been done during the past years, but most of them are concentrated on transition element substitution on the Mn site on divalent elements doped manganites systems, such as $La_{1-x}Sr_xMnO_3$ [11,12], $La_{1-x}Ca_xMnO_3$ [13–15] and $Pr_{1-x}Ca_xMnO_3$ [16], while relatively little work has been done on the effects of doping at the Mn site on monovalent element doped manganites. As for the monovalent element doped manganites ($La_{1-x}Li_xMnO_3$, $La_{1-x}Na_xMnO_3$, $La_{1-x}K_xMnO_3$ and $La_{1-x}Ag_xMnO_3$), it has been found that it is possible to obtain an equal amount of holes with a lower cation substitution resulting in smaller cation disorder [17,18]. In our previous work about $La_{1-x}Na_xMnO_3$ thin films synthesized by chemical solution deposition method, we found that it was possible to obtain a relatively high magnetoresistance (MR) value near room temperature due to similar ionic radius between Na^+ and La^{3+} [19]. In this paper, we further our study by substitution of Mn site with three different valence element (Mg, Cr and Ti) to study the electrical and magnetic properties of the derived films.

2. Experimental procedure

Nominal stoichiometric $La_{0.835}Na_{0.165}Mn_{0.9}RE_{0.1}O_3$ (RE=Mg, Cr, Ti) films were synthesized by the chemical solution deposition (CSD) method. The raw materials are lanthanum acetate, sodium acetate, manganese acetate, magnesium acetate, chromium acetate

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hydroxide and titanium n-butoxide. The substrate was $LaAlO_3$ (100) (LAO) single crystal. Propionic acid was used as chelating agent and butyl alcohol was used as solvent and a solution with a concentration of 0.2 M was used as precursor solution. A spin coater was used and the rotation speed was selected as 4000 rpm and the deposition time was 60 s. After each deposition process, the deposited layers were dried on a 300 °C preheated hot furnace for 30 min, and annealed at 800 °C for 2 h under a flowing O_2 environment. The deposition process was repeated for three times to obtain the final films with desired thickness. In order to depict clearly, we define here the sample $La_{0.835}Na_{0.165}MnO_3$ as LNMO, and the $La_{0.835}Na_{0.165}Mn_{0.9}RE_{0.1}O_3$ (RE=Mg, Cr, Ti) films as LNMMO, LNMCO and LNMTO respectively.

Conventional θ–2θ XRD studies on the films were carried out in Philips X'pert PRO X-ray diffractometer using CuKa radiation to investigate the crystalinity and crystal orientation of the films. Resistivity under zero and 3T magnetic field was measured by standard four-probe method. Magnetization measurements were carried out using a vibrating sample magnetometer (VSM) at the temperature range of 10–330 K. The MR ratio is defined as $MR=[(\rho_0-\rho_H)/\rho_0]\times 100\%$, where ρ_0 is the resistivity at zero field and ρ_H is the resistivity at the field H.

3. Results and discussion

The standard XRD θ–2θ patterns of all the films are shown in Fig. 1. It is observed that all the crystal structure can be indexed with a pseudocubic structure. Additionally, there are only (h00) peaks attributed to the films besides the peaks of LAO substrate, which implies that all the prepared films are highly *a*-axis oriented. From the insert of Fig. 1, it can be seen that the position of the (200) reflection peak of the sample LNMMO are almost the same as that of the sample LNMO. It is because the ionic radius of Mg^{2+} is identical with that of Mn^{3+}, no strong lattice effects would be introduced by Mg^{2+} substitution [20]. On the other hand, it can be observed that

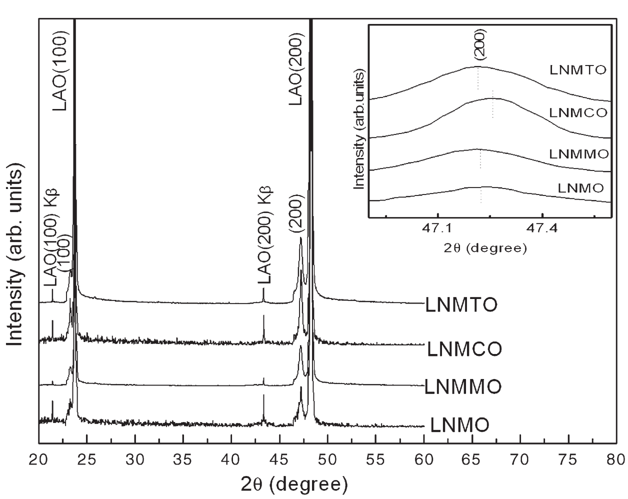

Fig. 1. X-ray diffraction patterns of the samples LNMO, LNMMO, LNMCO and LNMTO, respectively. The insert is the amplification of the (200) reflection peak.

Table 1
Some physical properties of all the samples

Sample name	LNMO	LNMMO	LNMCO	LNMTO
Concentration of Mn^{4+} ions (%)	33	43	33	23
T_c (K)	298	90	267	123
T_p (K)	321	/	295	161
E_{hop} (meV) from ln (ρ/T) versus 1/T	76	126	91	125

the (200) diffraction peak of the sample LNMCO is shifted to higher diffraction angle, while that of the sample LNMTO is shifted to lower diffraction angle. It means that the substitution of Cr^{3+} on Mn^{3+} site could decrease the lattice size because the ionic radius of Cr^{3+} (0.61 nm) is smaller than that of Mn^{3+} (0.65 nm), but the Ti^{4+} substitution would make the lattice expand. From the results of Kim MS [21] and Zhu XB et al [22], we think the Ti^{4+} ions mainly substitute the smaller Mn^{4+} ions in the sample LNMTO, which make the lattice constant increase and the XRD angle tends to lower degree. The calculated Mn^{4+} ion concentrations of all the samples are listed in Table 1.

Fig. 2 shows the temperature dependence of magnetization M(T) in both zero-field-cooling (ZFC) and field-cooling (FC) modes with an applied filed of 0.5T, and the applied magnetic field is parallel to the films surface. All the samples undergo a paramagnetic-ferromagnetic transition. The Curie temperature (T_c) was defined as the peak of dM/dT vs. T curve, and the detailed data are listed in Table 1. It can be clearly seen that the T_c and the maximum magnetization magnitude at 5 K of the sample LNMO is the highest, and those of the samples LNMMO, LNMCO and LNMTO are all decreased. It can be interpreted as the dilution of Mn^{3+}–O–Mn^{4+} network by the substitution of Mn site and the depression of the double exchange (DE) interaction [20,23]. Moreover, it can be seen that the FC and ZFC curves of the samples LNMO, LNMCO and LNMTO are identical, but the ZFC curves do not coincide with the FC curves at low temperatures for the sample LNMMO. This discrepancy between ZFC and FC curves is a characteristic of spin-glass cluster state, which shows the magnetic

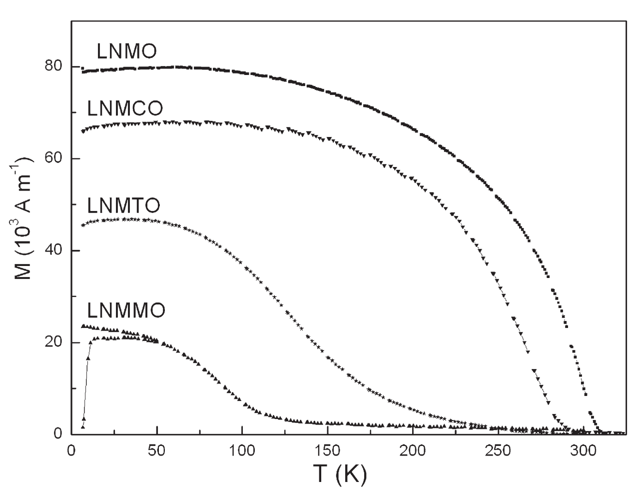

Fig. 2. The temperature dependence of magnetization for all the samples and the magnetic field is o.5 T.