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Preparation of epitaxial $La_{0.6}Ca_{0.4}Mn_{1-x}Fe_xO_3$ ($x = 0$, 0.2) thin films: Variation of the oxygen content

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Abstract

Perovskite thin films with a nominal composition of $La_{0.6}Ca_{0.4}Mn_{1-x}Fe_xO_3$ ($x = 0$, 0.2) were deposited by pulsed reactive crossed beam laser ablation. The film properties, such as electrical conductivity and magnetoresistance are studied as a function of the oxygen content and substrate type. The oxygen content of the thin films was determined by Rutherford Backscattering and controlled by varying the background gas pressure, pressure of the gas pulse and by using alternatively O_2 and N_2O as the gas pulse.

$LaAlO_3$ and $SrTiO_3$ were used as substrates at deposition temperature of 650 °C. The grown films were analyzed by X-ray diffraction in order to optimize the growth conditions, i.e. to obtain epitaxial thin films. Thin films doped with 20% Fe were grown under the same experimental conditions as the undoped LCMO films and the effect of the doping on the structural and transport properties of the thin films has been investigated.

The temperature of the metal–insulator transition was measured as a function of the oxygen content and substrate type.

Keywords: PRCLA; Oxygen stoichiometry; Manganites

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Contents

1. Introduction

A large research effort has been devoted in recent years to manganese oxides to take advantage of their interesting properties, i.e. metal to insulator transition and colossal magnetoresistance (CMR). Doped manganites, with general formula $Ln_{1-x}Ca_xMnO_3$ (Ln = Sr, Ca, La) have been intensively studied, as they are considered as potential candidates for industrial applications [1]. Increased attention has been given to the compound $La_{1-x}Ca_xMnO_3$, where the ions La^{3+} and Ca^{2+} have very similar ionic radius, e.g. 1.36 and 1.38 Å respectively. The Ca doped $LaMnO_3$ manganites have mixed valence Mn^{3+}/Mn^{4+} with the configuration $(t_{2g})^3(e_{g1})^1$ for Mn^{3+} and $(t_{2g})^3$ for Mn^{4+}. By changing the ratio La/Ca and by varying the temperature, the transport properties of the $La_{1-x}Ca_xMnO_3$ materials can be tuned from insulating to metallic state [2]. The magnetic properties can vary from paramagnetic, ferromagnetic to antiferromagnetic by changing the doping in the cationic site. In the ferromagnetic region, corresponding to a doping range $0.3 < x < 0.7$, a drop in the resistivity has been observed at the transition point from metal to semiconductor followed by the colossal magnetoresistive effect (CMR). The double exchange mechanism, which is often used to explain the CMR phenomena [3], consists of an exchange of the e_g electrons between neighboring Mn ions leading to parallel alignment of the spin, e.g. ferromagnetism ordering [4]. Another mechanism has been also suggested for a qualitative explanation of the experimental data and it consists in a strong electron–phonon interaction arising from the Jahn–Teller splitting of the outer Mn d level [5]. A localized lattice distortion induced by the Jahn–Teller effect was indicated to have a significant contribution to the CMR mechanism.

The double exchange mechanism is related to the Mn^{3+}–O^{2-}–Mn^{4+} bond distance and angle [6,7]. The physical properties of the manganites are determined by the doping level and by the cation radius [8]. The radius of the cationic atom influences the Mn^{3+}–O^{2-}–Mn^{4+} distance and the probability of electrons' transfer between the Mn ions. In this case, the tendency of an increasing transition point temperature with an increase of the radius size was observed.

Oxygen content in the films strongly affects the transport properties of the films. Several reports in the literature showed the importance of the oxygen in the transfer mechanism of the films [9,10]. After applying an annealing treatment, LCMO films exhibit a lower resistance and a more pronounced CMR effect.

A broadening of the ferromagnetic transition and a decrease in the magnetization was reported in the case of Fe doped compounds, $La_2MnCo_{1-x}Fe_xO_6$ ($0 < x < 0.5$), as Co is gradually substituted by Fe [11]. Several structural investigations on the Fe doped perovskites showed that the LCMO structure does not cause lattice distortion of the unit cell [1,12–14].

In this paper, we study the systems $La_{0.6}Ca_{0.4}Mn_{1-x}Fe_xO_3$ ($x = 0$, 0.2) processed as thin films by the PRCLA method and the effect of the substitution of Mn by another transition metal, e.g. 20% Fe.