

Determining the Valence State of Manganese Ions in Complex Oxides $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ ($x = 0.5, 0.7, 0.85, \text{ and } 0.9$) Based on $\text{Mn}2p$ and $\text{Mn}3s$ X-ray Photoelectron Spectra

K. A. Googlev^a, A. T. Kozakov^a, A. G. Kochur^b, A. V. Nikolskii^a,
V. I. Torgashev^c, and A. A. Zvolenskaya^c

^aResearch Institute of Physics, Southern Federal University, Rostov-on-Don, 344090 Russia

^bRostov State Transport University, Rostov-on-Don, 344038 Russia

^cFaculty of Physics, Southern Federal University, Rostov-on-Don, 344090 Russia

e-mail: kozakov_a@mail.ru

Abstract—The valence state of manganese ions in complex oxides $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ ($x = 0.5, 0.7, 0.85, \text{ and } 0.9$) is studied on the basis of $\text{Mn}2p$ and $\text{Mn}3s$ X-ray photoelectron spectra. It is shown that manganese ions have the valence of Mn^{3+} and Mn^{4+} in the studied compounds. The relative $\text{Mn}^{3+}/\text{Mn}^{4+}$ content is determined.

DOI: 10.3103/S1062873816060125

INTRODUCTION

Manganites of rare-earth elements are studied extensively since they exhibit large isotropic negative magnetoresistances and thus find various practical applications [1]. Research on their electron structure and other physical properties is driven by the current need for room-temperature microelectronic materials for magnetic recording heads, secure data storage, and so on. Rare-earth manganites with perovskite structure of the $R_{1-x}A_x\text{MnO}_3$ type (where R is a rare-earth ion, and A is a divalent element such as Sr, Ca, or Ba) are most promising in this respect. High temperatures of metal–semiconductor and ferromagnetic–paramagnetic phase transitions, in the vicinity of which the peak magnetoresistive effect is observed, are typical of rare-earth manganites with $R = \text{La}$ [1, 2].

EXPERIMENTAL

The ceramic $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ ($x = 0.5, 0.7, 0.85, \text{ and } 0.9$) samples studied in this work were prepared by means of solid-state reaction. X-ray photoelectron $\text{Mn}2p$ and $\text{Mn}3s$ spectra were measured using an ESCALAB 250 X-ray photoelectron microprobe. The lines were excited by X-ray monochromatized radiation with the energy of excitation of the AlK_α line (1486.6 eV). The surfaces of samples were additionally irradiated with a flux of slow electrons from an electron gun in order to compensate for charge effects. The bonding energy was calibrated against the C1s

carbon line, which was slightly above the background level.

The actual elemental composition of $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ samples was determined from $\text{La}3d$, $\text{Mn}2p$, $\text{Ca}2p$, and $\text{O}1s$ X-ray photoelectron spectra, according to the standard procedure in [3].

RESULTS AND DISCUSSION

It is known that $2p$ and $3s$ X-ray photoelectron spectra can be used to determine the valence state of ions of transition metals [3]. A number of studies revealing close agreement between the data on manganese ion valence and the local magnetic moment determined from $2p$ and $3s$ X-ray photoelectron spectra have already been conducted [4–10].

It was shown in [7–10] that $\text{Mn}2p$ spectra are sensitive to the temperature at which the samples are studied. A series of lowest-energy terms of manganese ions at different temperatures and their population were determined. The photoemission of electrons from these terms were $\text{Mn}2p$ spectra whose shapes varied greatly from one initial term to the other. The $\text{Mn}2p$ spectrum profile for an ion of a certain valence (Mn^{3+} , Mn^{4+}) at room temperature was a superposition of several electronic spectra. Each of these spectra corresponded to photoemission from one of the possible lowest-energy terms. The approach proposed in [7–10] allowed a good description of the experimental $\text{Mn}2p$ spectra. Since the $\text{Mn}2p$ spectra of $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ in this work were measured at room temperature, and the

Measured and nominal compositions of the studied $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ samples and their relative $\text{Mn}^{3+}/\text{Mn}^{4+}$ content

x	Actual measured composition	Relative Mn ion content	
		Mn^{3+}	Mn^{4+}
0.5	$\text{La}_{0.1}\text{Ca}_{0.3}\text{Mn}_{0.8}\text{O}_{3.8}$	0.746	0.254
0.7	$\text{La}_{0.15}\text{Ca}_{0.75}\text{Mn}_{1.3}\text{O}_{2.8}$	0.65	0.35
0.85	$\text{La}_{0.1}\text{Ca}_{0.7}\text{Mn}_{0.9}\text{O}_{3.3}$	0.415	0.585
0.95	$\text{La}_{0.05}\text{Ca}_{0.6}\text{Mn}_{0.75}\text{O}_{3.6}$	0.37	0.63

$\text{Mn}2p$ spectra of $\text{Mn}_2^{3+}\text{O}_3$ and $\text{Mn}^{4+}\text{SrO}_3$ (compounds that contain Mn^{3+} and Mn^{4+} ions, respectively) had already been measured at the same temperature and analyzed theoretically [7], we modeled the experimental $\text{Mn}2p$ X-ray photoelectron spectra of $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ as a sum of the experimental $\text{Mn}2p$ spectra of tri- and tetravalent ions. The $\text{Mn}2p$ X-ray photoelectron spectrum of $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ ($x = 0.5, 0.7, 0.85,$ and 0.9) samples was presented as a superpositioning of two contributions:

$$\text{Mn}2p(b, a_1, a_2) = a_1 \times \text{Mn}2p(\text{Mn}_2^{3+}\text{O}_3) + a_2 \times \text{Mn}2p(\text{Mn}^{4+}\text{SrO}_3), \quad (1)$$

where $\text{Mn}2p(\text{Mn}_2^{3+}\text{O}_3)$ and $\text{Mn}2p(\text{Mn}^{4+}\text{SrO}_3)$ are the spectra for tri- and tetravalent manganese ions. The fitting parameters were a_1 , a_2 , and b (the shift of the spectrum of trivalent Mn relative to that of tetravalent Mn).

The measured and the nominal compositions of the studied samples and their relative $\text{Mn}^{3+}/\text{Mn}^{4+}$ content are listed in the table. Figure 1 shows the experimental $\text{Mn}2p$ spectra and the spectra calculated using Eq. (1). It can be seen that the data are in close agreement.

We had already studied [7–10] the valence state of manganese in complex oxide compounds using $\text{Mn}3s$ spectra. It is known [11] that energy distance ΔE_{3s} between the high-spin and the low-spin components of $3s$ spectra varies in a roughly linear fashion along with the number of $3d$ valence electrons (provided that the $3s$ electrons are in the ground state). It was demonstrated experimentally and theoretically in [9] that the value of ΔE for the $3s$ level of manganese varies within the range of 4.9–5.1 eV at different relative concentrations of $\text{Mn}^{3+}/\text{Mn}^{4+}$. The experimentally determined energies of splitting between the high-spin and the low-spin components for di-, tri-, and tetravalent manganese are 6.4 ($\text{Mn}_2\text{V}_2\text{O}_7$), 5.4 (Mn_2O_3), and 4.4–4.5 eV (SrMnO_3) [7], respectively.

The energies of splitting between the high-spin and the low-spin components of the $\text{Mn}3s$ spectrum in the

studied $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ ($x = 0.5, 0.7, 0.85,$ and 0.95) system fall within the range of 4.7–5.1 eV [4–10]. This suggests that the manganese ions in this system are in their Mn^{3+} and Mn^{4+} valence states (Fig. 2). At the same time, it should be noted that these estimates do not allow us to determine the quantitative content of

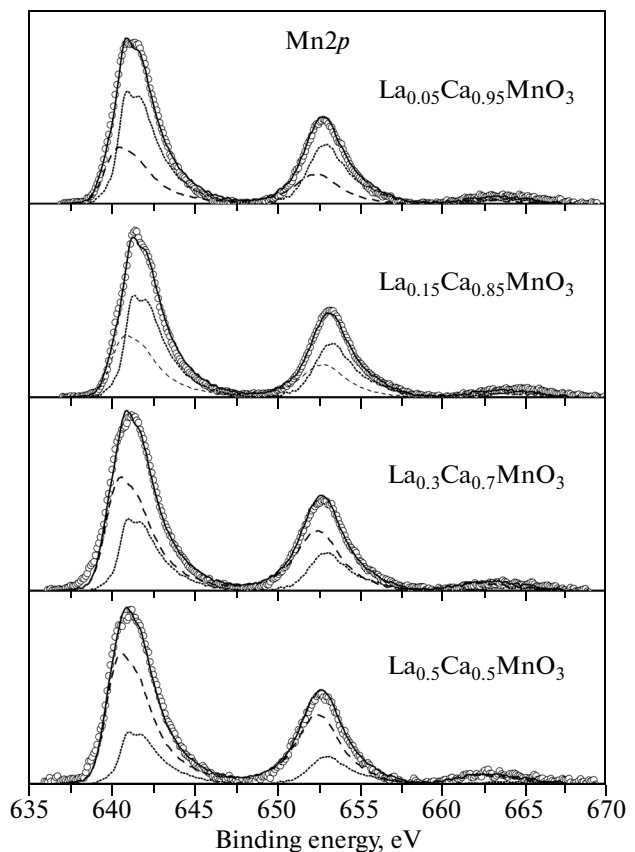


Fig. 1. Measured $\text{Mn}2p$ spectra of $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ samples (dots) and their fitting with Eq. (1) (solid curve). Dashed and dashed-and-dotted curves represent the contributions from $\text{Mn}_2^{3+}\text{O}_3$ and $\text{Mn}^{4+}\text{SrO}_3$.

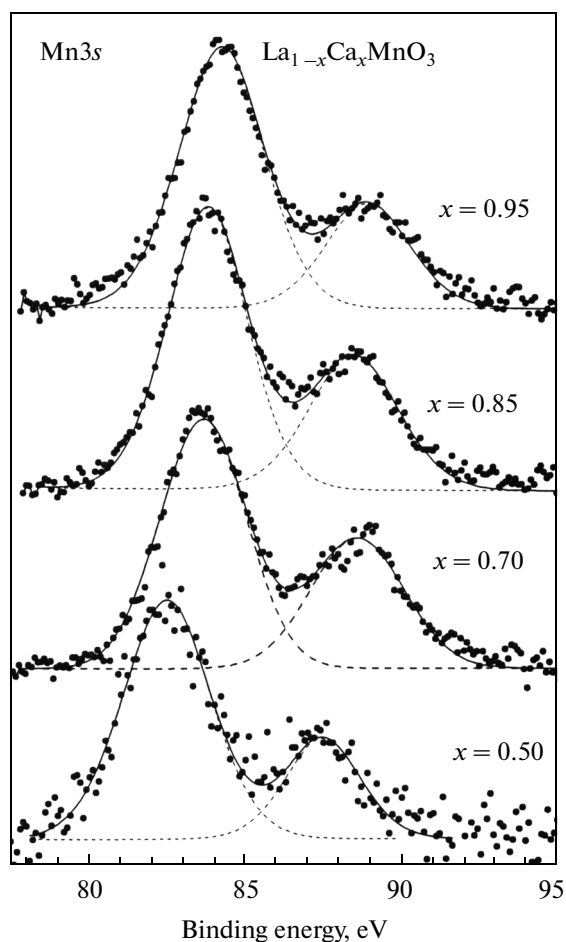


Fig. 2. Experimental Mn3s spectra of $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ ceramic samples.

different ions. It was demonstrated above that the relative content of ions in different valence states can be determined from Mn2p X-ray photoelectron spectra.

ACKNOWLEDGMENTS

This study was supported by the Ministry of Education and Science of the Russian Federation within the base part of the government assignment (project no. 1880).

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Translated by D. Safin