Dedicated to Professor Dr. Cozar Onuc on His 70th Anniversary

XPS INVESTIGATIONS OF La$_{0.67}$Sr$_{0.33}$Co$_{1-x}$Mn$_x$O$_3$ COMPOUNDS

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ABSTRACT. The electronic structure of the polycrystalline La$_{0.67}$Sr$_{0.33}$Co$_{1-x}$Mn$_x$O$_3$ perovskites with $0 \leq x \leq 0.5$ has been investigated by X-ray photoelectron spectroscopy (XPS). The valence band spectra shows several features, due to Mn 3d, Co 3d and extensively hybridized Mn3d-O2p and Co3d-O2p states, while the core level spectra show the presence of Co^{4+} and Co^{2+} states.

Keywords: Manganites, Cobaltites, X-ray photoelectron spectra

INTRODUCTION

The discovery of the colossal magnetoresistance (CMR) effect in the manganites R$_{1-x}$A$_x$MnO$_3$ (where R is lanthanum or a rare earth ion and A is a divalent alkali) [1] stimulated the interest to the new perovskite-type materials such as the cobaltites with a similar formula R$_{1-x}$A$_x$CoO$_3$ [2,3]. These latter compounds have technical application potential due to their high electrical and ionic conductivities, their use in ferroelectric thin film capacitors [4], in solid oxide fuel cells [5], as oxygen permeable membranes [6], as possible applications as magnetostrictive actuators [7], in thermoelectric elements [8] and as active catalysts [9]. The occurrence of CMR effect and of ferromagnetism in manganites had been attributed to the double-exchange (DE) interaction between Mn^{3+} and Mn^{4+} ions intermediated by 2p^6 O ions [1]. In the mentioned cobaltites, the origin of ferromagnetism seems to be different. LaCoO$_3$ is a nonmagnetic insulator at low temperature and SrCoO$_3$ is a long range ferromagnet [2]. Substitution of Sr^{2+} for La^{3+} in LaCoO$_3$ gives rise to a partial oxidation of Co^{3+} to Co^{4+} (3d^6) as in the similar formula manganites. This doping makes the material to segregate into hole-rich metallic ferromagnetic clusters and a hole-poor matrix similar to LaCoO$_3$ [10].

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A ferromagnetic order can occur, with a Curie temperature lower than 280 K, and the ferromagnetism is assumed to be of an itinerant electron type. [11]. For low Sr content (0.05 ≤ x ≤ 0.2) $La_{1-x}Sr_xCoO_3$ has spin-glass-like behaviour [12]. The striking feature of cobaltites, deciding their magnetic properties as compared to the CMR manganites, is the presence of the various spin states for Co^{3+} and Co^{4+} ions, i.e. they can be present in low-, intermediate- or high-spin state [2,3,10]. This fact is possible as a result of the competition between the comparable magnitudes of crystal field and intraatomic Hund energy, which dictates the occupation of the t_{2g} and e_g electron energy levels. The doped perovskites, $La_{1-x}Sr_xMnO_3$ [1,13] and $La_{1-x}Sr_xCoO_3$ [2,10-12] were extensively studied for the richness of their physical properties. For $x = 0.33$, the both systems exhibit long range ferromagnetic order. In the solid solution $La_{0.67}Sr_{0.33}Co_{1-x}Mn_xO_3$, a multitude of interactions between the magnetic ions, mediated by the oxygen ions is expected: Mn^{3+}–O–Mn^{4+}, Mn^{3+}–O–Mn^{3+}, Mn^{4+}–O–Co^{2+} and Mn^{4+}–O–Mn^{4+}, Co^{2+}–O–Co^{2+}, Co^{2+}–O–Mn^{3+} [14,15-17]. The chemical disorder as well as the magnetic ions disorder can cause major changes in the magnetoelectronic properties of these compounds.

Previously, we systematically studied the structural, electrical and magnetic properties of the compounds $La_{0.67}Sr_{0.33}Co_{1-x}Mn_xO_3$ with $0.5 ≤ x ≤ 1$ [15-17]. The samples, prepared by conventional ceramic method, were pseudo-cubic perovskites with slight rhombohedral distortions. The magnetic measurement indicated that the long range ferromagnetism from the optimal doped manganite $La_{0.33}Sr_{0.67}MnO_3$ is destroyed when more than half of the Mn ions are replaced by Co ions and a cluster glass magnetic state occurred (i.e. ferromagnetic clusters embedded in a non ferromagnetic matrix). This state was suggested by *M(H)* measurements and also by the frequency dependence of the ac susceptibility $\chi_{ac}(T)$ in the region of the freezing temperature T_f, described by a Vogel–Fulcher law that presumes correlations between spin clusters [15]. The samples showed low electrical resistivity with $\rho(T)$ curves indicating semiconductor behavior and rather high negative magnetoresistance, up to 18 % for $x = 1$. The resistivity is lower with increasing Co^{3+} ions content and its behavior in the high temperature range was attributed to a hoping mechanism in the presence of a charge disproportionation effect of Co^{3+} ions in Co^{2+} and Co^{4+} [18]. Besides these properties, $La_{0.67}Sr_{0.33}Co_{1-x}Mn_xO_3$ compounds were found [17] to show moderate magnetocaloric effect, comparable to that obtained in other perovskite-type compounds operating in the intermediate temperature range.

The present work is an extension of our previous studies [15-17] on the electrical and magnetic behavior of the system $La_{0.67}Sr_{0.33}Co_{1-x}Mn_xO_3$, to complete our data and to probe our assumptions with the information about the electronic structure of our samples. XPS technique [19] was used to investigate the chemical states of manganese and cobalt ions and the changes in the band structure in these compounds.

EXPERIMENTAL

The La$_{0.67}$Sr$_{0.33}$Co$_{1-x}$Mn$_x$O$_3$ samples were the same we used in our previous works [15-17], where the details of sample preparation and characterization measurements can be found. The samples were characterized by using magnetization, electrical transport and x-ray diffraction measurements.

The XPS measurements were performed by using an an ESCA (PHI 5600ci) spectrometer equiped with monochromatized Al Kα radiation with hν = 1486.6 eV. The measurements were performed under a base vacuum maintained below 10^{-9} mbar. In order to have samples with fresh surfaces the samples were cleaved in situ. The spectra were recorded at room temperature and calibrated against the Au 4f$_{7/2}$ signal from an Au foil (80.0 eV).

RESULTS AND DISCUSSION

The XPS valence band spectra of La$_{0.67}$Sr$_{0.33}$Co$_{1-x}$Mn$_x$O$_3$ perovskites show several features below 12 eV, as presented in Fig. 1a. The structure below 2 eV has a large Co 3d contribution at about 1 eV and hence decreases in intensity with the decrease of Co content [20]. In the spectral region between 2 eV and 5 eV there are several contributions from the Mn 3d (t_{2g}), Co 3d and of extensively hybridized Mn3d-O2p and Co3d-O2p states [21-23]. The third feature situated above 5 eV is associated with the O 2p bands.
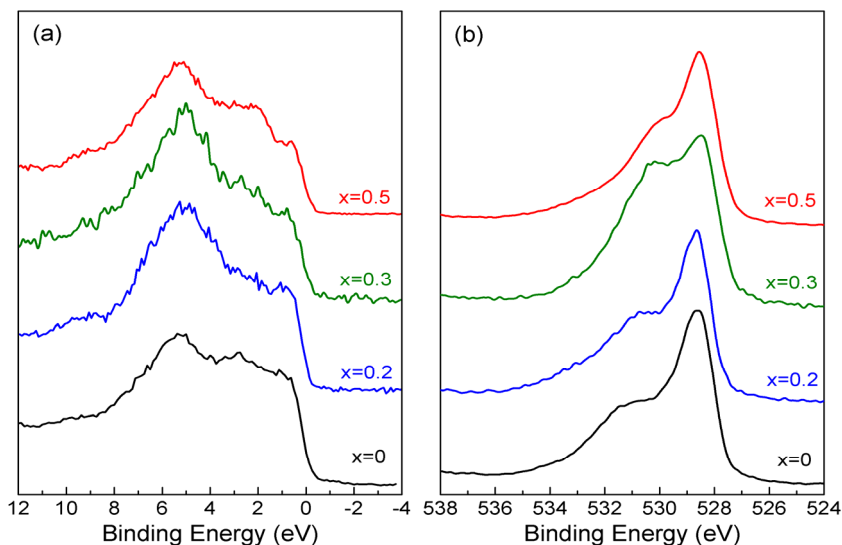

Fig. 1. a) XPS valence band spectra and b) XPS O 1s core level of La$_{0.67}$Sr$_{0.33}$Co$_{1-x}$Mn$_x$O$_3$ perovskites

The O 1s core level spectra shown in Fig. 1b present two distinct features for all the samples. The lower binding energy peak is generally assigned to the lattice oxygen (oxygen-metal bonds), while the higher binding energy peak is assigned to less electron-rich oxygen species and can be attributed to extrinsic effects such as defects in crystal lattice and surface contamination (adsorbed oxygen, hydroxyl, and carbonate species). For sintered samples, the relative contribution of this peak depends on the fabrication conditions and surface preparation.

The XPS spectra of the La 3d and La 4d levels, shown in Fig. 2, are very similar for all the samples. The La 3d photoelectron signal exhibits a spin orbit splitting of about 16.8 eV, typical for La^{3+} compounds. An additional split due to the transfer of an electron from the oxygen valence band to the empty La 4f level [24] leads to the double peak structures of nearly identical intensity of both the $3d_{3/2}$ and $3d_{5/2}$ levels. The separation between the main peak and the satellite peak does not change with the variation of Mn/Co content (~4 eV), suggesting that the interaction between the La ions and the transition-metal ions is very weak [24].
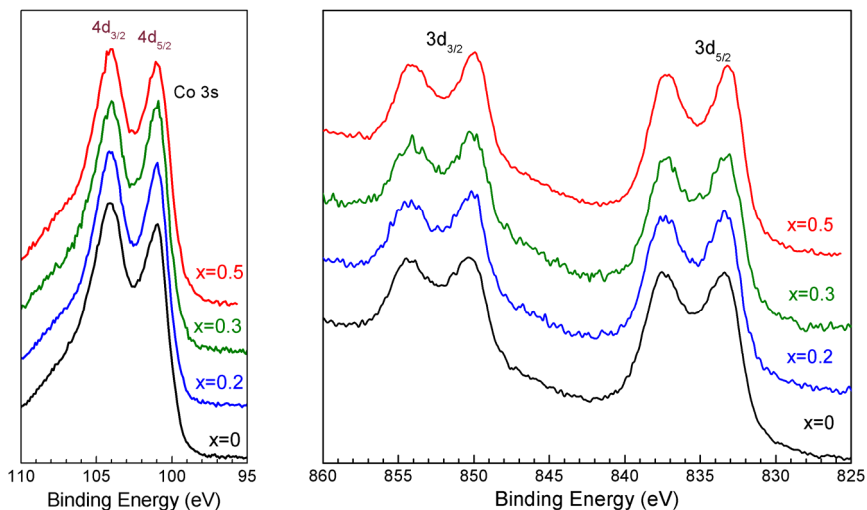

Fig. 2. XPS La 4d (left) and La 4d (right) core level spectra of $La_{0.67}Sr_{0.33}Co_{1-x}Mn_xO_3$ perovskites

The Mn 2p and Co 2p XPS spectra, shown in Fig. 3, provide valuable information about the transition metal ions valence state. There is no significant shift between the Mn 2p core level spectra of the investigated samples, which indicates that the Mn^{3+}/Mn^{4+} ratio does not change with the increase of Mn concentration. All spectra show a spin orbit splitting between the Mn $2p_{3/2}$ and Mn $2p_{1/2}$ levels of about 11.6 eV.
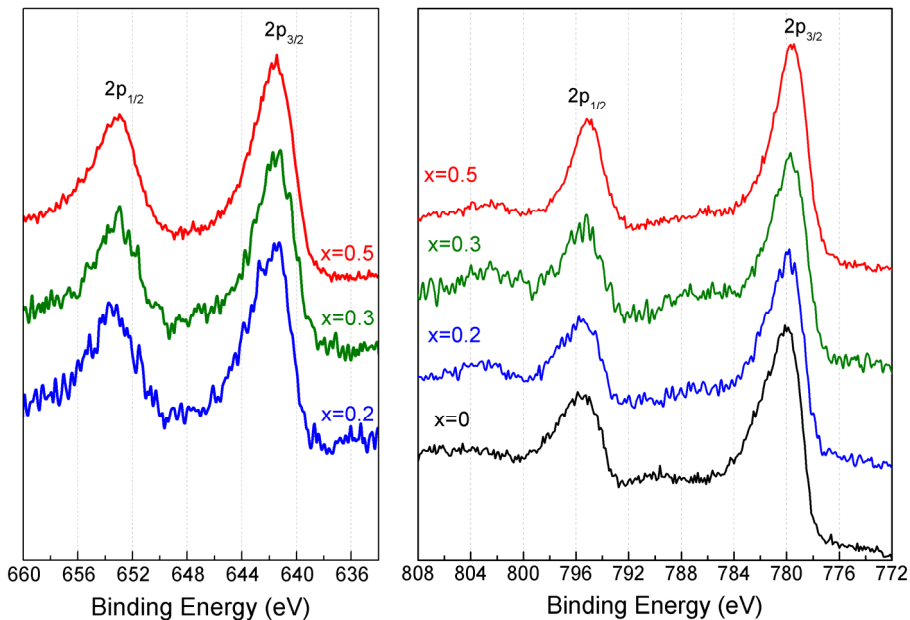
Fig. 3. XPS Mn 2p (left) and Co 2p (right) core level spectra of La$_{0.67}$Sr$_{0.33}$Co$_{1-x}$Mn$_x$O$_3$ perovskites

The Co 2p XPS spectra of all investigated samples present two main peaks situated at about 780 eV (2p$_{3/2}$) and 795.5 eV (2p$_{1/2}$) which indicates that Co is predominantly present as Co^{3+} state. The presence of a shoulder on the high energy side of the Co 2p$_{3/2}$ and Co 2p$_{1/2}$ components imply the presence of Co^{4+} states, with binding energies around 781.4 eV and 796.7 eV. The satellite features situated at 785-788 eV and 802-804 eV confirm also the presence of Co^{2+} ions in the samples with x>0 [25,26]. The satellite intensity in Co compounds is related to the spin states and increases with the increase of unpaired atomic electrons [27]. With the increase of Mn content one can notice a slight shift of the two main peaks towards lower binding energies, as well as a changes in widths and asymmetries. Fig. 4a shows the XPS spectra of Co 2p$_{3/2}$ core level after background removal, using a Shirley-type background shape [28]. By analyzing the binding energy and full width at half maximum (FWHM) of the Co 2p$_{3/2}$ core level we found that both decrease with the increase of Mn content, as presented in Fig. 4b and Fig. 4c, respectively.
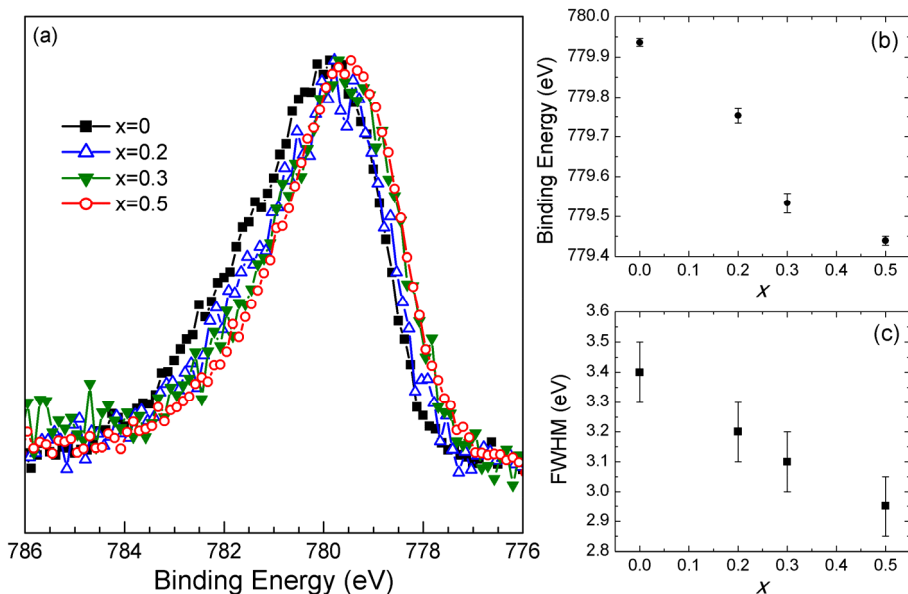
Fig. 4. (a) XPS spectra, (b) binding energies and (c) full width half maximum (FWHM) of Co $2p_{3/2}$ core level for $La_{0.67}Sr_{0.33}Co_{1-x}Mn_xO_3$ perovskites

CONCLUSIONS

The electronic structures of the $La_{0.67}Sr_{0.33}Co_{1-x}Mn_xO_3$ compounds were investigated by using the XPS technique. The XPS valence band spectra show several features below 12 eV, with several contributions from the Mn 3d, Co 3d and of extensively hybridized Mn3d-O2p and Co3d-O2p states in the spectral region between 2 eV and 5 eV. By analyzing the Mn 2p core level spectra we can conclude that the Mn^{3+}/Mn^{4+} ratio does not change with the increase of Mn concentration. The XPS Co 2p spectra confirm the presence of Co^{4+} and Co^{2+} states.

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