Journal of Molecular Structure 1073 (2014) 66–70

Contents lists available at ScienceDirect

Journal of Molecular Structure

journal homepage: www.elsevier.com/locate/molstruc

XPS study on $La_{0.67}Ca_{0.33}Mn_{1-x}Co_xO_3$ compounds

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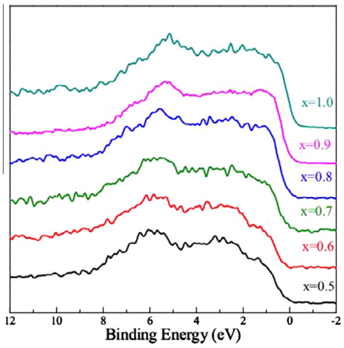
HIGHLIGHTS

- Electronic structure of $La_{0.67}Ca_{0.33}Mn_{1-x}Co_xO_3$ was investigated using XPS.
- Concentration of lattice oxygen relative to the total oxygen decreases with x.
- The Co 2p core level spectra indicate the presence of Co^{4+} and Co^{2+} states.
- La 3d, La 4d and O 1s XPS spectra show a shift toward higher BE when x increase.
- VB show features attributed to Mn 3d, Co 3d and hybridized Mn3d(Co3d)-O2p states.

GRAPHICAL ABSTRACT

XPS valence band spectra of $La_{0.67}Ca_{0.33}Mn_{1-x}Co_xO_3$ perovskites.



ARTICLE INFO

Article history:
Received 13 February 2014
Received in revised form 30 March 2014
Accepted 20 April 2014
Available online 26 April 2014

Keywords:
Cobaltites
Manganites
XPS spectra
Electronic properties

ABSTRACT

The electronic structure of the polycrystalline $La_{0.67}Ca_{0.33}Mn_{1-x}Co_xO_3$ compounds with $x = 0.5$, 0.6, 0.7, 0.8, 0.9 and 1 has been investigated by X-ray photoelectron spectroscopy (XPS). The valence band and the transition metal core level spectra were analyzed. Several contributions from the Mn 3d, Co 3d and of extensively hybridized Mn3d-O2p and Co3d-O2p states were found in the spectral region between 2 eV and 5 eV. The core level spectra show the presence of Co^{4+} and Co^{2+} states.

Introduction

The manganese and cobalt oxides, with general composition $R_{1-x}A_xMO_3$, where R is a La or a rare-earth ion, A is an alkaline-earth ion and M = Mn or Co, have been intensively investigated in the last years due to their interesting and intriguing physical properties such as colossal magnetoresistance (CMR), phase separation (PS), charge ordering (CO), orbital ordering (OO) and spin glass (SG) behavior and for their potential technical applications [1–11]. The physical properties of these compounds have been attributed to the complex electronic structure which arises from the strong competition between charge, orbital, lattice and magnetic degree of freedom [1,12–14]. It was shown that electronic and magnetic states of $(La_{1-x}R_x)_{0.7}Ca_{0.3}MnO_3$ where R = Y or Pr are related to the average radius, $\langle r \rangle$, of R^{3+} and Ca^{2+} ions [15]. The $\langle r \rangle$ value can determine the one-electron bandwidth. Small $\langle r \rangle$ values are favorable for the presence of charge ordering, which is present not only in antiferromagnetic region but can occur in ferromagnetic region too [16,17]. The physical properties of these

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http://dx.doi.org/10.1016/j.molstruc.2014.04.065
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materials can be modified by doping, for example with transition metals atoms, the behavior being strongly influenced by the concentration and the valence state of the dopant [18].

$RCoO_3$ is insulator, at low temperatures, with no magnetic order. In this case the cobalt state is Co^{3+} ($3d^6$) with the low-spin electronic configuration $t_{2g}^6 e_g^0$ (LS, $S = 0$). With increasing the temperature a gradually change of the spin state of Co^{3+} to the intermediate spin configuration $t_{2g}^5 e_g^1$ (IS, $S = 1$) or high spin state configuration $t_{2g}^4 e_g^2$ (HS, $S = 2$) appears. The redistribution of the electrons between the t_{2g} and e_g levels results from a competition between the crystal field splitting energy Δ_{cf} and the intra-atomic Hund exchange energy J_{ex} which have comparable values in cobaltites. The energy Δ_{cf} strongly depends on the Co–O bond length and therefore the balance between Δ_{cf} and J_{ex} can easily be changed by the temperature, external pressure or by a substitution of La for A ions [19–23]. It was shown that the doping with A^{2+} ions on rare earth site gives rise to the ferromagnetic order due to a partial oxidation of Co^{3+} in Co^{4+} ($3d^5$) [19–21].

On the other hand, in manganites, the presence of coexisting clusters of competing phases was reported. Generally, these phases are ferromagnetic embedded in different kinds of antiferromagnetic phases. It was shown that the appearance of these competing phases is a function of the overlap integral due to the mixing cations of different A sizes. It is accepted, in principle, that the double exchange ferromagnetic interaction occurs via the hopping of spin polarized e_g electrons between Mn^{3+} and Mn^{4+} [12]. Due to this interaction the electronic phase separation and the formation of ferromagnetic clusters in an antiferromagnetic matrix could be explained.

Previously we have studied the structural, electrical and magnetic properties of $La_{2/3}Ca_{1/3}Mn_{1-x}Co_xO_3$ compounds [22,23]. It was shown that the solid solutions $La_{2/3}Ca_{1/3}Mn_{1-x}Co_xO_3$, ($0.5 \leqslant x \leqslant 1$) form perovskite structure with rhombohedral symmetry. These materials are very complex systems with a multitude of interactions between the magnetic ions (Mn^{3+}, Mn^{4+}, Co^{2+}, Co^{3+}, Co^{4+}). The Co substitution for Mn induced a glassy magnetic behavior. The presence of correlated magnetic clusters at low temperatures was confirmed from magnetization measurements, from the frequency dependence of the ac susceptibility and from nonlinear ac susceptibility measurements. This state can be seen as composed from FM clusters (hole rich regions) embedded in some AFM (or PM) regions. At low temperatures the FM clusters extend and interact each other and the cluster glass state occurs. The resistivity is higher for low Co content in the samples and the magnetoresistance is only a few percents. This behavior was attributed to the disorder created in the system and to the grain boundary resistance. It was found that the resistance decreases and the magnetoresistance has higher values of 25%, for high Co content. It was suggested that the Co subsystem has the main role in electrical conduction. The electrical behavior was explained by hopping of the carriers in a Co^{3+} matrix in the presence of a disproportionate effect (for Co^{3+} ions in Co^{2+} and Co^{4+}) in the high temperature region.

There are many studies devoted to the structural, magnetic and magneto-transport properties of $R_{1-x}A_xMn_yM_{1-y}O_3$ where A = Ba, Ca, Sr and M = Co, Ni, Cr, Cu published in the last years but only few studies deal with their electronic structure. X-ray photoelectron spectroscopy (XPS) is one of the powerful tools to study the core levels of the materials. XPS spectra can provide important information on the electronic structure of manganese and cobalt perovskites. Core level XPS is sensitive to the chemical environment and can give information about the oxidation state of the probed ion, while the valence band region gives information about the total density of states.

In order to explain the interesting magnetic and transport properties of $La_{0.67}Ca_{0.33}Mn_{1-x}Co_xO_3$ compounds we have performed XPS measurements. Here the XPS studies on these compounds are reported.

Experimental

The samples were prepared by conventional solid state reaction, and they were found to be single perovskite phase in nature [22]. The XPS spectra were recorded using an ESCA (PHI 5600ci) spectrometer from Physical electronics with monochromatized Al Kα radiation with $h\upsilon = 1486.6$ eV. The measurements were done on fresh surfaces which were obtained by cutting the samples *in situ*. During measurements the pressure in the main chamber was maintained below 10^{-9} mbar. All spectra were recorded at room temperature and calibrated against the Au $4f_{7/2}$ signal from an Au foil (84.0 eV).

Results and discussions

The O 1s core level spectra for all the samples present two distinct peaks, as shown in Fig. 1.

The lower binding energy peak is generally assigned to the oxygen lattice (oxygen-metal bonds). There is a clear shift of this peak toward higher binding energy, as the Mn concentration increases, from 528.5 eV in $La_{0.67}Ca_{0.33}CoO_3$ to 529.1 eV in $La_{0.67}Ca_{0.33}Co_{0.5}Mn_{0.5}O_3$. This behavior is due to the changes in the first vicinity of the O atoms and is in agreement with previous reports regarding the O 1s binding energies in $La_{0.67}Ca_{0.33}MnO_3$ (529.1 eV [24,25]) and $La_{0.67}Ca_{0.33}CoO_3$ (528.6 eV [24,26]). The higher binding energy peak may be assigned to less electron-rich oxygen species. For sintered samples, the relative contribution of this peak depends on the fabrication conditions and surface preparation. High quality epitaxial films show a dominant low binding energy peak and very little emission for higher binding energies [24,27]. Therefore the high binding peak may be attributed to extrinsic effects such as defects in crystal lattice and surface contamination (adsorbed oxygen, hydroxyl, and carbonate species). After background removal, using a Shirley-type background shape [28], the O 1s core-level spectra were fitted using five components: a contribution from the bulk-bound O^{2-} with binding energy between 528.4 eV and 529.1 eV, a second contribution at about 528.7 eV assigned to surface oxygen species [29], a third contribution at 531.0 eV coming from hydroxyls species OH^-, a forth carbonyl contribution at about 532.2 eV (C 1s peak showed also a small component at 287 eV), and a fifth contribution at 533.5 eV probably from adsorbed molecular water. The full width at half maximum (FWHM) was considered between 1 and 1.5 eV for each component. The curve fitting

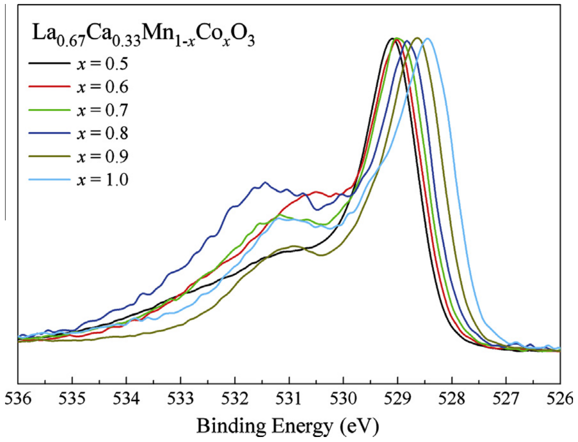

Fig. 1. XPS O 1s core level spectra of $La_{0.67}Ca_{0.33}Mn_{1-x}Co_xO_3$ perovskites.