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Degradation of $La_{0.8}Ca_{0.2}MnO_3$ single crystal surface: Electron spectroscopy studies

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Abstract

The electronic structure of degraded (as grown and chemically polished) and ion-sputtered $La_{0.8}Ca_{0.2}MnO_3$ single crystal surfaces has been studied by X-ray photoemission and Auger electron spectroscopy techniques. XPS spectra of deep core levels (Mn2p, O1s, La3d, La4d) were taken from as grown, chemically polished and cleaned in UHV by Ar^+ ion-bombardment surfaces. XPS data show different oxidation state of Mn and La ions on the degraded and ion-sputtered surfaces of the manganite crystal. $Mn2p_{3/2}$ line width and energy position suggest mixed valence state of the manganese ions at the degraded and ion-sputtered crystal surfaces.

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1. Introduction

Mixed-valence perovskite manganites have attracted considerable attention during last years due to their unique magnetic and transport properties. An interest to these compounds has increased since the discovery of colossal magnetoresistance (CMR) [1–5]. This magnetic-field-induced insulator–metal transition is explained with double exchange (DE) mechanism [6,7] based on the exchange of electrons between Mn^{3+} and Mn^{4+} ions through the oxygen site. Doping of manganites by alkaline-earth or oxygen atoms can change Mn^{4+}/Mn^{3+} ratio that define transport and magnetic properties as well as magnitude of the CMR effect. From this point of view, it is interesting to know the influence of various sample treatments on Mn oxidation states.

At some circumstances manganites can be in a phase separation (PS) state observed also in similar perovskite structures (for example, HTSC). Two different scenarios of PS are considered in theory: the impurity or electronic phase separation. The presence of easily diffusing oxygen ions plays an important role in the first PS scenario. At the meantime, problems of defect structure in oxygen deficient manganites and anion role in the doped manganites transport and magnetic properties formation are not quite clear. According to investigations on $LaMnO_{3-d}$ and $La_{1-x}Sr_xMnO_{3-d}$ compounds [8,9] the oxygen deficiency leads to the Mn^{2+}-oxygen vacancy-Mn^{2+} cluster formation. Such cluster formation shifts the Mn^{3+}/Mn^{4+} ion ratio into the phase separation region. In some papers on $LaMnO_{3+d}$ ceramics [10–12] the determining role of vacancies in La- and Mn-sublattices was proposed: the cation sublattice has vacancies and the actual stoichiometry of these compounds is $La_{(1-d/3)}Mn_{(1-d/3)}O_3$. Besides, as reported by Roosmalen and co-workers, sample treatments in air lead to positive d values, while treatments in oxygen lead to negligibly small d values. However, it is difficult to take into account the processes at the grain boundaries in such polycrystalline systems. Only a few studies were performed on single crystalline samples. For example, in Ref. [13] the degrading role

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of oxygen vacancies in $La_{0.85}Sr_{0.15}MnO_{3-d}$ single crystal was experimentally observed.

In this paper, we present electron spectroscopy studies of $La_{0.8}Ca_{0.2}MnO_3$ single crystalline samples. Because of surface sensitivity photoemission spectroscopy may give information on manganese oxidation states in the topmost layers. The correlation between surface and bulk electronic structure (and consequently transport properties) is very important for tunneling and microcontact investigations. As a rule, in perovskite structures (manganites or cuprates) the surface layer is degraded in respect of transport and magnetic properties. The surface degradation may be caused just by interaction with atmosphere components (water vapours and so on). From this point of view, "degradation" (as we used this term in the current paper) means the modification of transport and magnetic properties of the manganite surface layers relative to the bulk ones. Thus, initially we have "degraded" surface on as grown and polished $La_{0.8}Ca_{0.2}MnO_3$ crystal. We have tried to look for possible changes in the electronic structure (especially in manganese and oxygen derived states) after removal of the topmost "degraded" layer of as grown and electrochemically polished single crystal. Besides, this work was also motivated by observation of the electric current switching effect on normal metal-degraded $La_{0.8}Ca_{0.2}MnO_3$ surface heterocontacts [14]. A typical example of the observed effect is presented in Fig. 1: strong current injection at certain polarity of the electric field can change the transport properties of the manganite surface layers (see inset in Fig. 1). As a result, metastable low (LRS) and high resistive states (HRS) can be identified in current–voltage characteristics of the heterocontact. Temperature dependence of the heterocontact resistance shown in Fig. 1 demonstrates the difference in resistance and Curie temperature for HRS and LRS. One can see that Curie temperature is substantially higher for the manganite crystal in LRS. These experimental observations evidence charge state reconstruction (and possibly a phase separation) in the surface layers of the contact region under influence of the electric field. In this scenario, the main role can play easily diffusing ions, so one may anticipate the presence of mobile oxygen ions and oxygen vacancies in topmost layers of manganite crystal.

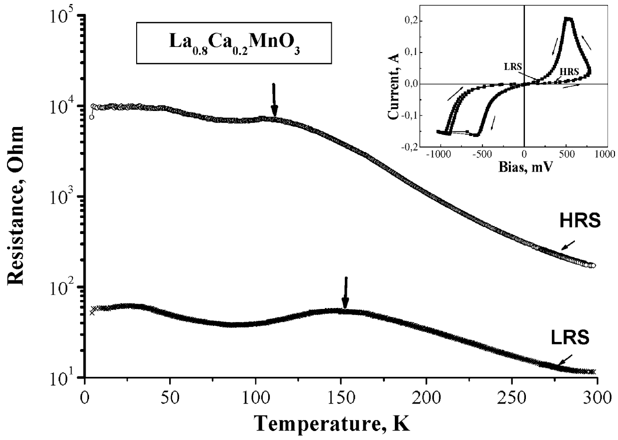

Fig. 1. Temperature dependence of low and highly resistive states in a $La_{0.8}Ca_{0.2}MnO_3$–Ag heterocontact. The arrows show the corresponding Curie temperatures. *Inset*: an example of *I–V* characteristic of a $La_{0.8}Ca_{0.2}MnO_3$–Ag film heterocontact with reproducible LRS–HRS switchings. The arrows show the voltage scanning direction. In this example electric field strength $E(J)$ is directed towards the crystal surface, when the applied voltage is negative and it is directed in reverse when the applied voltage is positive. $E(J) = J \times \sigma$ (J, current density; σ, conductivity).

2. Experiment

The electronic structure of as grown, electrochemically polished and ion-sputtered $La_{0.8}Ca_{0.2}MnO_3$ surfaces has been investigated by Auger-electron spectroscopy (AES) and X-ray photoemission spectroscopy (XPS) with ESCALAB-5 spectrometer (VG Scientific). In this work, we used $La_{0.8}Ca_{0.2}MnO_3$ single crystal grown by technique described in Ref. [15] and tested by X-ray spectral and structural analysis. The samples used for spectroscopy studies were cylinders 4 mm in diameter and 3 mm in height with axis perpendicular to (0 0 1) plane. Electrochemical polishing of $La_{0.8}Ca_{0.2}MnO_3$ crystal was performed in acid solution of H_3PO_4 (65%), H_2SO_4 (20%) and H_2O (15%).

AES and XPS spectra were measured from (0 0 1) plane of degraded (as grown and electrochemically polished) and ion-sputtered $La_{0.8}Ca_{0.2}MnO_3$ single crystal surfaces. Ar^+-bombardment was carried out in preparation chamber of electron spectrometer (base pressures in analytical and preparation chambers were 2×10^{-10} and 8×10^{-10} mbar, respectively). Ar^+ ions with energy of 3.5 keV were used for etching, pressure in the preparation chamber upon ion treatments was 1.5×10^{-6} mbar. The sputtering rate at these parameters was approximately 5 Å/min. For electronic structure analysis photoemission lines of deep core levels (namely O1s, Mn2p, Mn3s, La4d and La3d) were exploited. XPS core level spectra presented in this work were recorded at photon energy corresponding to Mg Kα radiation ($h\nu = 1253.6$ eV) with electron spectrometer pass energy of 20 eV. The total energy resolution during XPS measurements (electrons plus photons) was approximately 1.2 eV. The electron spectrometer was calibrated by valence band and core level XPS spectra taken from Au foil so that Au E_F corresponded to a zero of binding energy (BE) and $Au4f_{7/2}$ maximum—83.95 ± 0.1 eV.

3. Electron spectroscopy data

XPS and AES spectra of degraded $La_{0.8}Ca_{0.2}MnO_3$ samples (both polished and as grown single crystals) before ion-bombardment demonstrated strong signals from oxygen and carbon contaminants as well as La and Mn peaks. Thus, ion-bombardment in these studies was used for two different purposes—to remove carbon contamination and look for changes of the electronic structure going from the fully degraded (on the top of the sample) to bulk layers of single