JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS Vol. 10, No. 4, April 2008, p. 857 - 859

XPS and resistivity studies on Y-Ca-Mn-Al perovskites

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The $Y_{0.67}Ca_{0.33}Mn_{1-x}Al_xO_3$ perovskites with x ≤ 0.2 were prepared by standard solid state reaction. The samples crystallize in an orthorhombic type structure having Pnma space group. The magnetic measurements show that the Mn^{4+} content increases as the aluminum substituted gradually manganese. The XPS study shows a decrease of the Mn3s splitting as the Al content increases and in addition the Mn3s and O1s core levels are shifted to higher binding energies. Magnetoresistivity measurements were also performed. These were correlated with data obtained from XPS and magnetic studies.

(Received February 25, 2008; accepted April 2, 2008)

Keywords: Manganite, Spin-glass, Electronic structure, Magnetoresistivity, Complex susceptibility

1. Introduction

The physical properties of manganese-type perovskites, $A_xR_{1-x}MnO_3$, where R is a rare earth and A an alkaline earth, are of interest both from fundamental and technical reasons. Their properties are mainly determined by manganese ions, which change their valence states as the rare earths are gradually replaced by alkaline earths.

In this paper we present the studies performed on Y-Ca-Mn-based perovskites. The $Y_{0.67}Ca_{0.33}MnO_{3-\delta}$ crystallizes in an orthorhombic type structure having Pnma space group [1-4], in which the oxygen content is close to theoretical value, $\delta=0$ [5]. Previous studies on $Y_{0.67}Ca_{0.33}Mn_{1-x}Al_xO_3$ perovskites show that for $x \le 0.2$ these crystallize in the same type structure as the end series compound [6]. When increasing the aluminum content, the cell volumes decrease compared to that of $Y_{0.67}Ca_{0.33}MnO_3$ and the bond angles between Mn-O1-Mn and Mn-O2-Mn slightly increase tending towards to the ideal value (180^0). The magnetization measurements suggest the presence of mictomagnetic type behavior.

In this paper we analyze the electronic structures, magnetoresistivities and magnetic susceptibilities of $Y_{0.67}Ca_{0.33}Mn_{1-x}Al_xO_3$ perovskites.

2. Experimental

The $Y_{0.67}Ca_{0.33}Mn_{1-x}Al_xO_3$ perovskites with x=0; 0.1 and 0.2 were prepared by standard ceramic procedure [6].

The XPS measurements were performed with a PHI 5600ci multi-technique spectrometer with monochromatic Al K_α radiation, with a resolution of about 0.4 eV. The spectrometer was calibrated using an Au foil as a reference sample (the binding energy of the Au $f_{7/2}$ core level is 84.0 eV). To get a surface free of contaminations, the sample was fractured in situ.

The temperature dependences of the ac susceptibilities were analyzed with an Oxford Instruments-type equipment, in the temperature range $10 \le T \le 50$ K, at the frequency of 10^2, 10^3, $5x10^3$ and 10^4 Hz, in a field of 1 Oe.

The resistivities were measured in a cryogen-free magnet cryostat CFM-7 (Cryogenic Ltd.), by a conventional four probe method in temperature range $145 \text{ K} \le T \le 300$ K and in field up to $\mu_0H = 7$ T.

3. Experimental results

The Mn3s core level spectra are presented in Fig. 1. The spectra consist of two lines that are attributed to exchange interactions of 3s and 3d electrons [7 - 17]. The exchange splitting, ΔE_{3s}, in the sample with x=0 is 4.98 eV which corresponds with a formal valence of +3.336 [8]. The exchange splitting decreases as the aluminum content increases. Thus for x=0.1 this is 4.9 eV and for x=0.2 a value 4.88 eV was obtained, which corresponds to the formal valences +3.34 and +3.40, respectively. The increases of the formal valences are confirmed by the data obtained from paramagnetic measurements [6]. These evidence also an increase of the Mn^{4+} content when the Al^{3+} content is higher, from 33.6 % (x=0) to 34.4 % (x=0.1) and 39.5 % (x=0.2). There is a shift of Mn3s lines to higher binding energies as the aluminum content increases. Thus the Mn3s core lines shift from 83.62 eV (x=0) to 83.97 eV (x=0.1) and 84 eV (x=0.2). The above chemical shift, is a result of changing the composition. An increase in binding energies of Mn3s lines were also observed in $SrMnO_3$-based perovskites [18, 19].

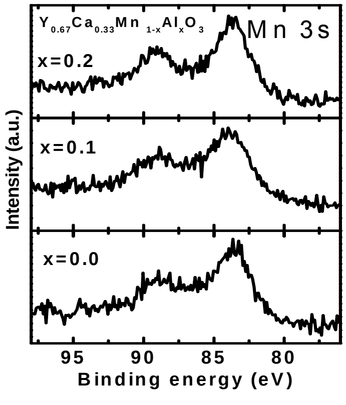

Fig. 1. The Mn3s XPS spectra at room temperature.

The O1s core level spectra are presented in the Fig. 2. There are two O1s lines. The line at lower binding energy is due to the oxygen in crystal lattice, while that at higher energy can be attributed to the presence of O^{2-} or OH^- ions [15, 20, 21]. The maxima in the O1s core line, involved in Mn-O binding, are shifted to higher energies from: 529.1 eV (x=0) to 529.32 eV (x=0.1) and 529.41 eV (x=0.2). These shifts are parallel to those shown for Mn3s core lines.

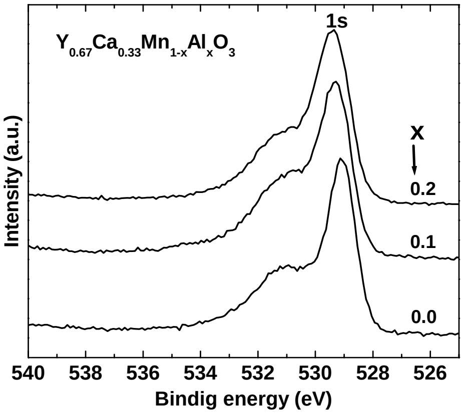

Fig. 2. The O1s XPS spectra at room temperature.

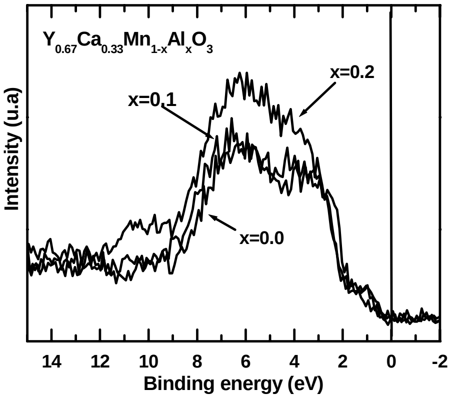

Fig. 3. The XPS valence band spectra.

The XPS valence band spectra are plotted in the Fig. 3. These are similar to those of other manganese type perovskites [9, 22, 23]. The energy level situated below the Fermi level at, 1.5 eV, is due to the Mn3d e_g electrons. The line located at 3 eV was attributed to the hybridizations of 3d (t_{2g}) Mn with O2p band [22]. The maxima situated between 6 eV and 7 eV are due to the hybridizations of the Mn3d and O2p bands [23]. The last line of the valence band, situated at 10.5 eV, can be correlated with the presence of some impurities, structural defects or OH^- absorptions [22]. When increasing the aluminum content, the intensities of the lines located at the 1.5 eV and 3 eV decrease, and those situated at 6 and 7 eV and mainly at 10.5 eV increases. The increase of the intensities of lines situated, at higher binding energies can be correlated with an increase of the number of oxygen defects or OH^- ions in the samples.

The real components of the magnetic susceptibilities show maxima at the Curie points – Fig. 4. The maxima are shifted to lower temperatures as the frequencies decrease. Also, there is an increase of the intensities maxima when the frequencies increase, behavior which is typical for a spin glass or mictomagnetic system. This confirms our previous results [6].

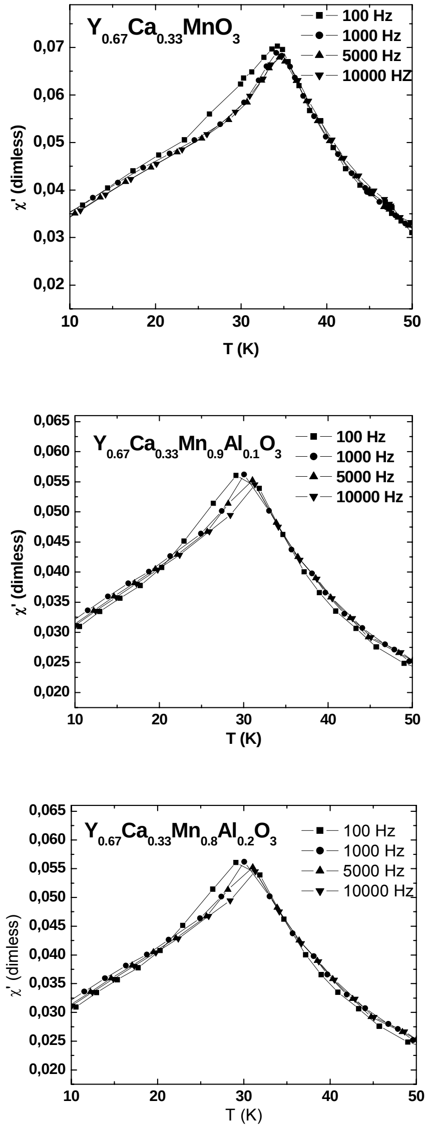

Fig. 4. Temperature and frequency dependences of the real components of the magnetic susceptibilities in a field of 1 Oe.

The temperature dependencies of resistivities for the samples with x=0.1 and x=0.2, in the range 220-295 K, are plotted in Fig. 5. Although the resistivities are rather high, there is a decrease of their values as compared with the sample having x=0. In the temperature range 270-290 K the resistivities are little dependent on temperature. The magnetoresistivities were also studied – Fig. 6. The small negative magnetoresistivities of the samples at T = 255 K and 285 K can be correlated with the paramagnetic state of the samples - Fig. 6.

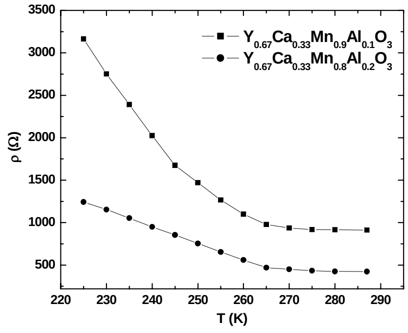

Fig. 5. Temperature dependences of the resistivities.

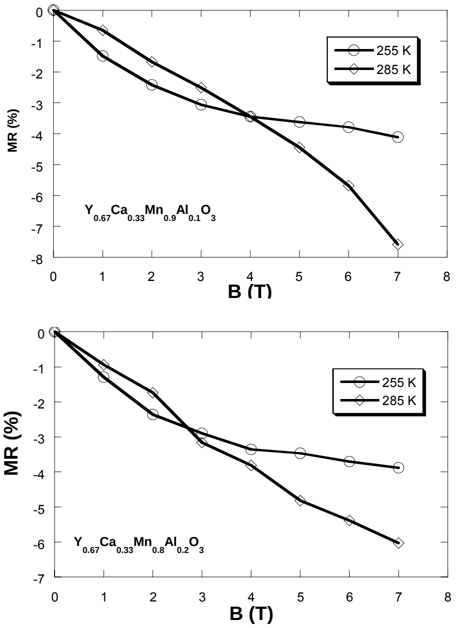

Fig. 6. The field and temperature dependences of the magnetoresistivities.

4. Conclusions

The formal valences of manganese ions, determined from the exchange splittings of 3s-3d electrons band, ΔE_{3s}, increase in the same way like those obtained from magnetic measurements. The decrease of the intensity of the line characteristic of e_g electrons level, situated at 1.5 eV below the Fermi level, confirms the above data. The Mn3s and O1s core levels shifts to higher binding energies by changing the composition. The number of structural defects increases parallely with that of aluminums ions, as showed by changes in the O1s core level spectra. The real components of the magnetic susceptibilities show a typical behavior characteristic for spin glass or mictomagnetic systems. The resistivities of the samples decrease with the increase of the aluminum content, compared to those of the end series compound. Near the room temperature (270÷290 K), the resistivities are little temperature dependent. The small negative magnetoresistivities in the studied temperature range can be correlated with the paramagnetic state of the studied samples.

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