STRUCTURAL PECULIARITIES AND PROPERTIES OF (La,Sr)(Mn,Me)O_3 (Me=Cu,Cr)

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Abstract: Actual oxidation state of doped ions in $La_{0.7}Sr_{0.3}Mn_{1-x}Me_xO_{3\pm\delta}$ systems (Me = Cu, Cr; $0\leq x\leq 0.15$) has been determined based on the analysis of structural, magnetic and resonance properties of these materials. It has been shown that for copper-substituted manganites there are two regions of concentrations with different magnetic properties. At $x\leq 0.05$ they are homogeneous ferromagnetics with a small variation of magnetic parameters, while at $x>0.05$ they become substantially inhomogeneous and both the saturation magnetization and Curie temperature significantly decrease with x increasing. The chromium-substituted compounds are homogeneous ferromagnetics in all investigated concentration range. These results can be explained only in supposition of divalent copper ions and trivalent chromium ones, which was verified and confirmed experimentally.

Keywords: Lanthanum Strontium Manganite/SOFC Cathode/Magnetic Sensors/Oxidation State/Rietveld Refinement/Magnetization/Ferromagnetic Resonance

1. INTRODUCTION

Lanthanum strontium manganites (LSM) are very attractive both from scientific and practical point of view as cathode materials for solid-state fuel cells as well as materials with colossal magnetoresistance for magnetic sensors [1]. Substitutions in manganese sublattice allow essentially changing the properties of LSM. On the one hand, such substitutions can modify the conductivity, phase stability, thermal expansion coefficient, chemical compatibility with YSZ and redox behavior of LSM cathode for SOFC. On the other hand, they can lead to a reduction in Zener energy of the double exchange and allow a controlling decrease of the operating magnetic fields.

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The aim of the present work is to specify the charge compensation mechanisms occurring at substitutions in the manganese sublattice, basing on the analysis of the interrelation between structural, magnetic, and resonance properties of the $La_{0.7}Sr_{0.3}Mn_{1-x}Me_xO_{3\pm\delta}$ (Me=Cu, Cr) compounds.

2. EXPERIMENTAL PROCEDURE

The polycrystalline $La_{0.7}Sr_{0.3}Mn_{1-x}Me_xO_{3\pm\delta}$ (Me = Cu, Cr) samples were prepared using solid state sintering technique. The X-ray investigations were carried out on DRON 4-07 diffractometer (Co $K\alpha$ radiation). The structural parameters were refined by Rietveld full-profile. Shannon's system of ionic radii was used to analyze the crystal structure aspects of the substitutions. Magnetic properties were measured in Quantum Design MPMS-5S SQUID magnetometer. Ferromagnetic resonance (FMR) spectra were recorded using X-band RADIOPAN spectrometer on the samples of parallelepiped shape (1×1×5 mm), with the magnetic field along the long axis.

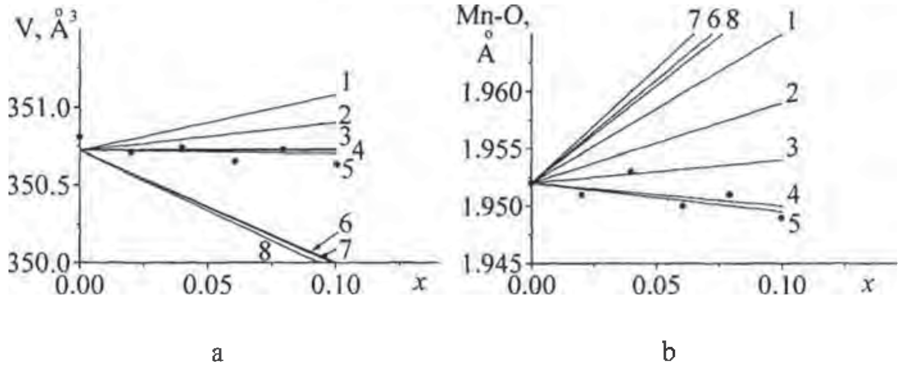
3. RESULTS AND DISCUSSION

The structure parameters of copper-containing manganites were in detail investigated in our previous work [2]. The analysis of experimental data allowed to reveal the most probable mechanisms of charge compensation during the substitutions in manganese sublattice and to calculate the percentage of Mn^{4+} ions, one of the important parameters governing magnetic properties of doped manganites [3]. It also allowed us to come to the conclusion about 2+ oxidation state of copper in $La_{0.7}Sr_{0.3}Mn_{1-x}Cu_xO_{3\pm}$ (LSMCu) compounds. The process of charge compensation can be described by *two* simultaneous reactions of substitution with the formation of oxygen vacancies:

$$2Mn^{3+} \rightarrow Mn^{4+} + Cu^{2+} \text{ and } 2Mn^{3+} \rightarrow 2Cu^{2+} + V_O^{\bullet\bullet}. \qquad (1)$$

In this work, an analogous procedure was applied to the investigation of chromium-containing manganites. Fig. 1 shows the experimental dependence (points) of the unit cell volume and the interatomic Mn–O distance of $La_{0.7}Sr_{0.3}Mn_{1-x}Cr_xO_{3\pm}$ (LSMCr) on chromium content as well as theoretical curves calculated using the assumptions of different charge compensation mechanisms at substitution of Cr for Mn. In these calculations, we assumed that Mn is in oxidation states 3+ and 4+ only [1,3], while chromium can be in different states (2+, 3+, 4+, 5+, 6+). It is clear from Fig. 1, that experimental data can be fairly good fitted with theoretical curves (4) and (5), which correspond to the following mechanisms of charge compensation:

$$2Mn^{3+} \rightarrow Mn^{4+} + Cr^{2+} \quad \text{(II) or } Mn^{3+} \rightarrow Cr^{3+} \quad \text{(III)}$$

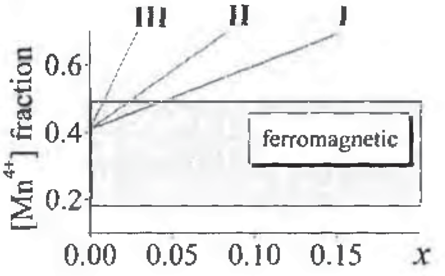


a b

Figure 1. Experimental dependences of the unit cell volume (a) and the interatomic Mn–O distance (b) of $La_{0.7}Sr_{0.3}Mn_{1-x}Cr_xO_{3\pm\delta}$ *samples on the chromium content (points) and theoretical curves calculated in supposition of the different charge compensation mechanisms for substitution of Cr for Mn:* $3Mn^{4+} \rightarrow 2Mn^{3+} + Cr^{6+}$ *(1);* $2Mn^{4+} \rightarrow Mn^{3+} + Cr^{5+}$ *(2);* $Mn^{4+} \rightarrow Cr^{4+}$ *(3);* $2Mn^{3+} \rightarrow Mn^{4+} + Cr^{2+}$ *(4);* $Mn^{3+} \rightarrow Cr^{3+}$ *(5);* $2Mn^{3+} \rightarrow 2Cr^{2+} + V_O^{\bullet\bullet}$ *(6);* $Mn^{4+} \rightarrow Cr^{2+} + V_O^{\bullet\bullet}$ *(7);* $2Mn^{4+} \rightarrow 2Cr^{3+} + V_O^{\bullet\bullet}$ *(8).*

To make a choice between these mechanisms the investigation of magnetic properties of the materials should be carried out. Keeping this goal in mind, we calculated the fraction of Mn^{4+} ions ($[Mn^{4+}]/[Mn_{total}]$) in $La_{0.7}Sr_{0.3}Mn_{1-x}Me_xO_{3\pm\delta}$ as a function of x, based on the Eqs. (I)-(III). It is known [1,3] that a homogeneous ferromagnetic phase can exist in Sr-containing manganites if the Mn^{4+} content is in the 0.18-0.50 range. Out of this range, the tendency to antiferromagnetic ordering predominates, which gives rise to antiferromagnetism or more complex types of magnetic ordering [3]. However it should be noted that the results of such analysis are valid only if the magnetically active ions are manganese ones only, while doped ions do not participate in magnetic interaction and stand as nonmagnetic impurity [1,2]. The situation when Me ions take part in magnetic interaction should be considered separately.

For LSMCu system, homogeneous ferromagnetism can exist only below $x = 0.05$ (see Fig. 2). At $x > 0.05$ more complex types of magnetic ordering should be expected [1,3]. The dependence of Curie temperature T_C on x (Fig. 3, curve 1) and ferromagnetic resonance data (Fig. 4a) are in good agreement with this statement. For the samples with $x = 0$ and 0.025, the resonance spectra consist of a single line with parameters that correspond to the ferromagnetic state of manganites and similar to those obtained in other works for $La_{0.7}Sr_{0.3}MnO_3$ samples [4]. Meanwhile the magnetic resonance spectra for the samples with $x > 0.050$ consist of two well-defined absorption lines, which correspond to two different magnetic phases.



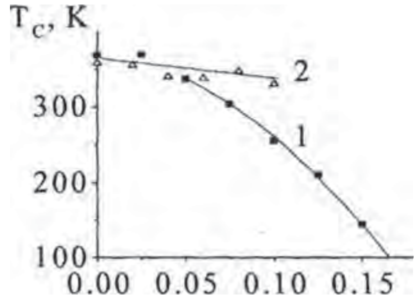


Figure 2. Mn^{4+} fraction for LSMCu (I) and LSMCr (II, III) samples. The lines correspond to the charge compensation mechanisms described by Eqs (I) – (III), respectively. Hatched area shows the region of existence of a homogeneous ferromagnetic phase.

Figure 3. Curie temperature as a function of doped ions content (x) for LSMCu (1) and LSMCr (2) samples.

Fig. 2 also demonstrates the magnetic diagram of chromium-containing compounds as a function of the Cr concentration calculated from Eqs. (II) and (III). The calculations were based on the supposition that chromium ions do not participate in the magnetic interaction. As can be seen from the figure, in both cases we should expect a magnetic inhomogeneity above $x \approx 0.03$. However the experiments showed that up to $x = 0.10$ the compounds behaved as homogeneous ferromagnetics. This was supported by the facts that the shape of FMR spectra remained practically the same (Fig. 4b) and T_C only slightly changed with the variation of chromium content (Fig. 3, curve 2).

The evidence of weak influence of Cr substitution on magnetic properties of the manganites was obtained in several previous works [5,6]. Based on the results of magnetic measurements the authors [5] suggested that Cr ions in these compounds are in 3+ oxidation state and participate in double exchange, which is the base of manganite ferromagnetism. The results obtained in this work showed that only such an approach could explain all complex of structure and magneto-resonance properties of LSMCr system. As is seen from the above analysis, other mechanisms, including those connected with the appearance of chromium ions in the oxidation state other than 3+, cannot describe the behavior of chromium-substituted manganites. The most likely reason for the participation of chromium ions in magnetic interaction inside Mn-O-Cr chain is the identity of electronic configurations ($t_{2g}^3e_g^0$) of Mn^{4+} and Cr^{3+} ions [5].

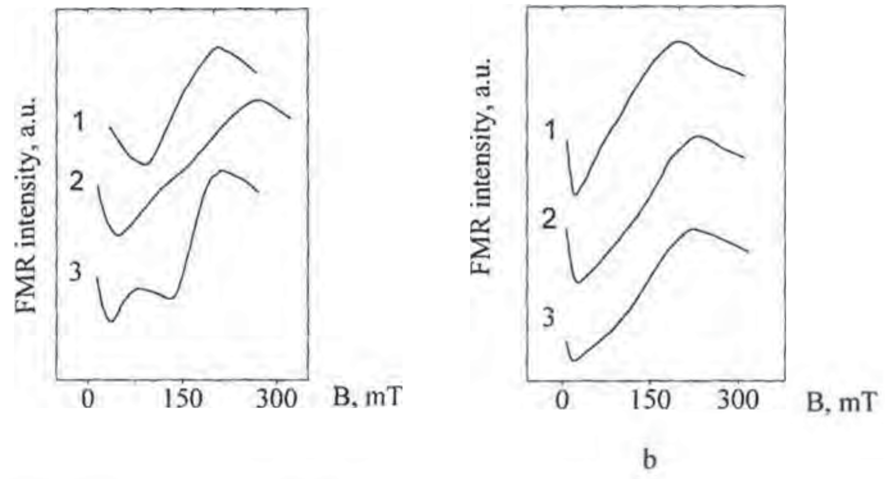


Figure 4. FMR spectra (T = 77 K) of : a) LSMCu samples with different copper content: x = 0.025 (1); 0.050 (2); 0.075 (3); b) LSMCr samples with different chromium content: x = 0 (1); 0.04 (2); 0.08 (3).

To confirm the existence of double exchange between Mn and Cr ions the following additional argument can be presented. If the ferromagnetic double exchange dominates in manganite system, the substitution of Cr for Mn should weakly affect the magnetism due to the participation of chromium ions in the double exchange. However, if the double exchange is not a dominant interaction, the substitution of Cr for Mn should lead to the enhancement of ferromagnetism. Such effects were observed in several works devoted to the investigation of Mn → Cr substitution on properties of weakly ferromagnetic manganites [7] and antiferromagnetic charge-ordered manganite compounds [8].

4. CONCLUSIONS

Based on the results of comprehensive analysis of dependences of structural, magnetic and resonance properties of $La_{0.7}Sr_{0.3}Mn_{1-x}Me_xO_{3\pm\delta}$ (Me = Cu, Cr) compounds on *x* the following conclusions have been made:

1. The mechanism of charge compensation in copper substituted manganites has to include participation of oxygen vacancies and is described by *two* simultaneous reaction of substitution of Cu for Mn: $2Mn^{3+} \rightarrow Mn^{4+} + Cu^{2+}$ and $2Mn^{3+} \rightarrow 2Cu^{2+} + V_O^{\bullet\bullet}$. Realization of such mechanism in $La_{0.7}Sr_{0.3}Mn_{1-x}Cu_xO_{3\pm\delta}$ leads to the transition from homogeneous ferromagnetism to inhomogeneous magnetism (two magnetic phases state) with *x* increasing.

2. Chromium ions in LSMCr system are in 3+ oxidation state and take part in ferromagnetic double exchange with manganese ions. The Mn → Cr substitution should weakly affect the magnetic properties of manganites if their basic state is ferromagnetism, but should lead to the appearance or enhancement of ferromagnetism for manganites with another types of magnetic ordering. It has been shown experimentally that FMR spectra as well as Curie temperature of $La_{0.7}Sr_{0.3}Mn_{1-x}Cr_xO_{3\pm\square}$ remain practically unchanged up to $x = 0.10$.

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