Kyiv, Ukraine
June 06-10, 2004

NATO Advanced Research Workshop

Fuel Cell Technologies: State and Perspectives

The Program

CO-DIRECTORS

N. Sammes, USA, and O. Vasylyev, Ukraine

INTERNATIONAL ORGANIZING COMMITTEE

N. Sammes (USA), O. Vasylyev (Ukraine), L. Blum (Germany), A. Demin (Russian Federation), W. Kriven (USA), N. Orlovskaya (USA), S. Skinner (UK), V. Skorokhod (Ukraine)

LOCAL ORGANIZING COMMITTEE

V. Burdin, M. Brychevs'ky, M. Golovkova, O. Koval I, M. Lugovy, I. Okun'

CONFERENCE SECRETARIAT

O. Koval (Ukraine), A. Smirnova (USA)

SPONSORING ORGANIZATIONS

The North Atlantic Treaty Organization
European Office of Aerospace Research and Development
Center for Advanced Materials and Smart Structures, North Carolina A&T State University
Connecticut Global Fuel Cell Center
Frantcevych Institute for Problems of Materials Science
Zirconia Ukraine Ltd.

Structural Features and Properties of (LaSr)(MnCu)O_3

O. V'yunov[(1)], A. Belous[(1)], O. Yanchevskii[(1)], A. Tovstolytkin,[(2)] V. Golub[(2, 3)]

[(1)] *V.I.Vernadskii Institute of General & Inorganic Chemistry, Ukraine*
[(2)] *Institute of Magnetism, Ukraine*
[(3)] *AMRI, University of New Orleans, USA*

Lanthanum strontium manganites (LSM) are very attractive from both scientific and practical point of view as cathode materials for solid oxide fuel cells and materials with colossal magnetoresistance for magnetic sensors. Partial substitution of manganese ions by copper ions allows a substantial change of the properties of LSM. For example, such substitution modifies conductivity, phase stability, thermal expansion coefficient, chemical compatibility with YSZ, redox behavior of LSM cathode for SOFC, and leads to a reduction of Zener energy of the double exchange providing lower working magnetic fields. But so far there is no clarity as for the copper oxidation state, which is one of the factors that determines the $[Mn^{4+}]/[Mn^{3+}]$ ratio, the oxygen nonstoichiometry γ and, as a result, the magnetic properties of lanthanum manganites.

The aim of the present work is to determine the actual oxidation state of copper ions and its correlation with magnetic properties of $(La_{0.7}Sr_{0.3})(Mn_{1-x}Cu_x)O_{3-\gamma}$ system ($0 \le x \le 0.15$).

Bulk samples of $(La_{0.7}Sr_{0.3})(Mn_{1-x}Cu_x)O_{3-\gamma}$ were prepared by the solid-state reaction technique. The phase purity and the crystal structure were examined by powder x-ray diffraction. Unit cell parameters, Mn-O distances and Mn^{4+}-O-Mn^{3+} bond angles were deduced from the Rietveld refinement of the XRPD data. The magnetization properties were investigated measured using Quantum design MPMS-5S SQUID magnetometer. ESR spectra were recorded at 9,2 GHz. It has been shown that solid solutions are formed in the whole investigated range of copper concentrations ($0 \le x \le 0{,}15$), and their unit cell volume varied with x according to Vegard's law. There are two regions of concentrations with different character of the saturation magnetization dependence on x. At $x \le 0{,}05$ the saturation magnetization changes slightly, whereas at $x > 0.05$ it significantly decreases with x. These results can be explained in supposition of divalent copper ions in the $(La_{0.7}Sr_{0.3})(Mn_{1-x}Cu_x)O_{3-\gamma}$ system, which was verified and confirmed experimentally.

Keywords: lanthanum strontium manganite, SOFC cathode, magnetic sensors, copper, oxidation state, Rietveld refinement, magnetization, ESR spectra.