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ScienceDirect
Solid State Ionics 179 (2008) 1101 – 1107
SOLID STATE IONICS
www.elsevier.com/locate/ssi

Electrical conductivity and oxygen non-stoichiometry of the double B mixed perovskite series $La_{0.6}Ca_{0.4}Mn_{1-y}Me_yO_{3-\delta}$ with Me=Fe, Co, Ni and $x=0–0.6$

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Received 14 July 2007; received in revised form 3 April 2008; accepted 18 April 2008

Abstract

Double B perovskite-type series in the system $La_{0.6}Ca_{0.4}Mn_{1-x}Me_xO_{3-\delta}$ with Me=Fe, Co, Ni and $x=0–0.6$ were synthesized in air by solid state reactions at 1200 °C from simple oxides and $CaCO_3$. Almost single phase compositions with small impurities (3–5%) were formed. Replacement of Mn with Me-cations is accompanied by a considerable decrease of electrical conductivity of the prepared ceramics. Lower conductivities of the Me containing compositions compared to $La_{0.6}Ca_{0.4}MnO_{3-\delta}$ are explained by stronger polarization of the -$Mn^{(\alpha+\gamma)+}$-$O^{\alpha-}$-$Me^{(\alpha-\gamma)+}$-$O^{\alpha-}$- fragments of the –$O^{\alpha-}$-$Mn^{\alpha+}$–$O^{\alpha-}$-$Mn^{\alpha+}$–$O^{\alpha-}$-$Mn^{(\alpha+\gamma)+}$-$O^{\alpha-}$-$Me^{(\alpha-\gamma)+}$-$O^{\alpha-}$- chains in comparison with the -$O^{\alpha-}$-$Mn^{\alpha+}$-$O^{\alpha-}$-$Mn^{\alpha+}$-$O^{\alpha-}$- chains without Me-cations, because of different electronegativity of Me and Mn. The double exchange theory gives strong explanation for this phenomenon. Type and level of the electrical conductivity of the $La_{0.6}Ca_{0.4}Mn_{1-x}Me_xO_{3-\delta}$ series are the functions of the $[Mn^{4+}]/[Mn^{3+}]$ and $[Me^{3+}]/[Me^{2+}]$ ratios. Mn^{4+} and Me^{2+}-cations are possible point defects which determine the p- and n-type conductivity of compositions, respectively.

Keywords: $La_{0.6}Ca_{0.4}Mn_{1-x}Me_xO_{3-\delta}$, Electrical conductivity; Oxygen non-stoichiometry

1. Introduction

The most appropriate material to be used as cathode with zirconia electrolyte was found to be the porous A-site deficient $(La_{1-x}Sr_x)_{1-\alpha}MnO_3$ (LSM). A quantitative mechanistic interpretation of the behavior of LSM-YSZ composite cathodes is not clear up to now [1], but it is known that the loss of voltage is the highest on cathodes of electrolyte supported cells such as LSM//8YSZ//Ni/YSZ. The highest electrical conductivity of the $La_{1-x}M_xMnO_3$ ceramics at 100 °C, about 150 $S*cm^{-1}$, was found for $x=0.3$ [2].

Some of the double B mixed perovskites $A'_{1-x}A''_xMn_{1-y}B_yO_3$ where A' is rare-earth, A'' is alkali-earth and B is 3d transition metal are described in the literature [3–11] as materials with interesting magnetic and electrical properties. Only few of the above-mentioned publications [5–7,11] report conductivity data of the Mn–Co and Mn–Ni double B mixed perovskites. These were measured under different conditions with different A-site occupations and hence it is difficult to compare their values depending on B-site occupation. No publications of the double B mixed perovskites containing Fe and Mn at B-sites were found. The behavior of the investigated compositions at high temperatures and different oxygen partial pressure conditions is practically unknown.

Taking into consideration the above-mentioned facts, the aim of this work was to compare the electrical conductivity of the double B mixed $La_{0.6}Ca_{0.4}Mn_{1-x}Me_xO_{3-\delta}$ (Me=Fe, Co, and $x=0–0.6$) perovskite series with the same A-site occupancy depending on their B-cation occupation, temperature and oxygen concentration in

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0167-2738/$ - see front matter
doi:10.1016/j.ssi.2008.04.025

surrounding gas atmosphere. The investigated systems were chosen because Ca^{2+} and La^{3+} ions have almost similar ionic radii (Ca^{2+}(XII) = 1.34 Å, La^{3+}(XII) = 1.36 Å, Ba^{2+}(XII) = 1.61 Å, Sr^{2+}(XII) = 1.44 Å). The concentration of Fe, Co and Ni was preferred in the given range $x=0$–0.6, because our previous investigation [12] shows existence of $La_{0.6}Ca_{0.4}Mn_{1-x}Ni_xO_{3-d}$ solid solutions in this range only and thus the Co- and Fe- containing double B compositions are compared with the Ni-cation containing substances. The properties of the analogous Ni-containing series are partially used in this article, for comparison.

2. Experimental

The series of the double B mixed perovskite-type $La_{0.6}Ca_{0.4}Mn_{1-x}Me_xO_{3-\delta}$ compounds with Me═Fe, Co, Ni and $x=0$–0.6 were synthesized in air by a ceramic technique. The corresponding amounts of La_2O_3, $CaCO_3$, Mn_2O_3, Fe_2O_3, Co_2O_3 and NiO containing at least 99.9% of the basic substances were milled together with ethanol in a planetary-type mill for 24 h. The formed slurries were dried and the obtained mixtures of oxides were heated at 1200 °C for 20 h. The products then were milled for 24 h again. After drying, the formed powders were pressed into bars along with 4 Pt wires, and sintered in air at 1200 °C for 33 h. The sintered ceramic samples were used for further conductivity and oxygen non-stoichiometry measurements.

Phase analysis was carried out by means of the powder diffraction technique using a Siemens D5000 X-ray diffractometer (Cu K_α-radiation, $\theta/2\theta$-scanning mode, step width of 0.02°, counting time per step 7 s).

Oxygen non-stoichiometry and electrical conductivity have been investigated in Ar/O_2 gas flow with oxygen partial pressures of 2–10^5 Pa and temperatures between 20 and 1000 °C using solid electrolyte coulometry and potentiometry techniques as described elsewhere [13]. Electrical conductivity was measured by means of DC 4-point method simultaneously with the oxygen non-stoichiometry. The measured conductivity values were corrected to zero-porosity as described elsewhere [14]. Argon with $pO_2=1.5$ Pa was used as carrier gas. An electrochemical titration was used to adjust the oxygen concentration in the reactor.

The oxidation states of Ni and Mn cations in Ni-containing series were estimated by XANES (X-ray Absorption Near Edge Structure) in HASYLAB DESY Hamburg on Beamlin E4 in transmission mode. Monochromatic X-rays were produced on Si (111) twin crystal at an energy step of 1.5 eV.

3. Results and discussion

3.1. Oxidation states of the transition metal cations in $La_{0.6}Ca_{0.4}Mn_{1-x}Ni_xO_{3-\delta}$

The room temperature XRD patterns of the $La_{0.6}Ca_{0.4}Mn_{1-x}Fe_xO_{3-\delta}$, $La_{0.6}Ca_{0.4}Mn_{1-x}Co_xO_{3-\delta}$ and $La_{0.6}Ca_{0.4}Mn_{1-x}Ni_xO_{3-\delta}$ powders after synthesis at 1200 °C indicate the formation of single phase compositions with orthorhombic perovskite-type structure. Sometimes small (3–5%) impurities were observed of prepared substances.

$La_{0.6}Ca_{0.4}Mn_{0.9}Co_{0.1}O_3$ and $La_{0.6}Ca_{0.4}Mn_{0.8}Co_{0.2}O_3$ powders were pure perovskites with orthorhombic structure. The additional reflections of Ca_3CoMnO_6 appear at the patterns in $La_{0.6}Ca_{0.4}Mn_{1-x}Co_xO_3$ with $x=0.3$–0.6. Besides, the peaks of CoO were detectable at patterns for $x=0.5$–0.6. The amount of impurities, which is increasing with Co content, was estimated in the range 1–5% mass. $La_{0.6}Ca_{0.4}Mn_{0.9}Fe_{0.1}O_3$ and $La_{0.6}Ca_{0.4}Mn_{0.8}Fe_{0.2}O_3$ powders display orthorhombic perovskite structure. Besides, unidentified impurity peaks with intensities of 3–5% are detected in the patterns. $La_{0.6}Ca_{0.4}Mn_{1-x}Fe_xO_3$

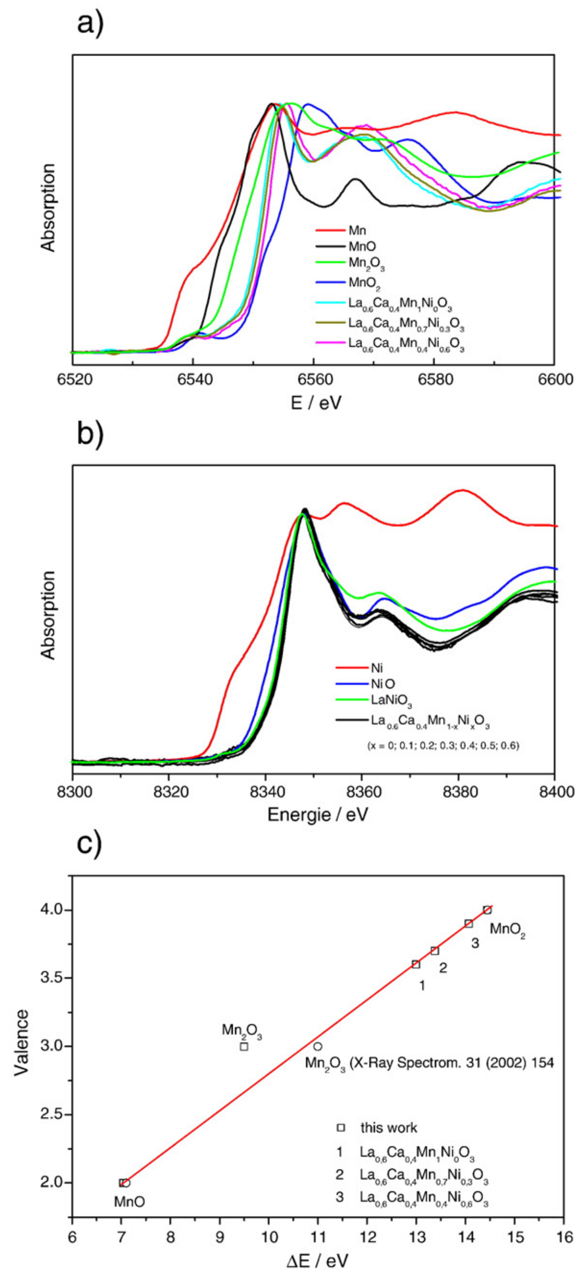

Fig. 1. Normalized Mn (a) and Ni (b) K-edge XANES-spectra of Mn, MnO, Mn_2O_3, MnO_2, $La_{0.6}Ca_{0.4}Mn_1Ni_0O_3$, $La_{0.6}Ca_{0.4}Mn_{0.7}Ni_{0.3}O_3$, $La_{0.6}Ca_{0.4}Mn_{0.4}Ni_{0.6}O_3$, Ni, NiO, $LaNiO_3$, and $La_{0.6}Ca_{0.4}Mn_{1-x}Ni_xO_3$ ($x=0$–0.6) as also Mn valence for $La_{0.6}Ca_{0.4}Mn_1Ni_0O_3$, $La_{0.6}Ca_{0.4}Mn_{0.7}Ni_{0.3}O_3$, and $La_{0.6}Ca_{0.4}Mn_{0.4}Ni_{0.6}O_3$ samples (c).