The Structure of Nanopowders and High Temperature Ceramics of Lanthanum Manganite with Excess Manganese

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The results of structure study of (La_{1-x}Sr_x)_{1-y}Mn_yO_{3+δ} and (La_{1-x}Ca_x)_{1-y}Mn_yO_{3+δ} manganites without (x=0) and with excess manganese (x=0.2) in the nanosize powders and ceramics sintering at 1450-1500 °C were presented. It is found that excess manganese isn’t integrated to a lattice of manganite and segregates to the near-surface region, but its presence leads to obtaining of smaller size of single phase nanoparticle of ~15-17 nm in a powder; the prevention of decomposition of stoichiometric manganite phase and forming of internal multilayer structure of ceramics grain with layer size of 70-140 nm at high temperature sintering.

Keywords: Lanthanum manganite, Magnetic nanoparticles, Nanostructure, Magnetic multi-layers.

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1. INTRODUCTION

Magnetic properties of manganites at the nanometer scale comprise an issue of great interest nowadays. A number of investigations of the grain size effect on magnetic and magnetoresistive properties of the hole-doped lanthanum manganite La-A-Mn-O (A = Ca, Sr, Ba) nanoparticles have been published recently [1-5]. In addition to this the effect of particle size on magnetoresistive properties of these materials with excess manganese has been researched too [6-8]. In previous papers [8,9] it is shown than in the (La_{1-x}Sr_x)_{1-y}Mn_yO_{3+δ} and (La_{1-x}Ca_x)_{1-y}Mn_yO_{3+δ} ceramics samples with excess manganese (x=0.1 and 0.2) sintered at 1450-1500 °C the release of excess manganese on the grain boundary and the intensive grain grown are observed. Furthermore, these samples exhibit an internal nanosize grain structure which leads to significant changes of magnetoresistive properties of manganite ceramics.

In this work the results of structural study of a behavior of excess manganese in the evolution process from powder to ceramics sintered at high temperature are presented.

2. SAMPLE PREPARATION AND EXPERIMENTAL DETAILS

The manganite nanosize powders of (La_{0.63}Sr_{0.37})_{1-x}Mn_xO_{3+δ} and (La_{0.63}Ca_{0.37})_{1-x}Mn_xO_{3+δ} (x = 0 and 0.2) marked as LSMO-0, LSMO-2, LCMO-0 and LCMO-2, respectively, were produced by the co-precipitation method from nitrate solutions and synthesis using related cold isostatic pressing (1GPa) and calcination at 600 °C [10,11]. To obtain the ceramics, the powders compacted in pellets by pressure of 1 GPa were sintered in air in two stages: at 1000°C for 5 h and at 1500°C for 2 h (for LCMO-0 and LCMO-2 at 1450 °C) during slow heating and cooling (100°C/h). To recover the oxygen stoichiometry, the samples were annealed a temperature of 300 °C in air for 5-6 h. To elucidate the internal grain structure, the ceramic samples were cleaved; the cleaved surfaces were thermally etched at 1000 °C for 3 h. The microstructure of ceramic samples were investigated by a scanning electron microscope (SEM) JEOL JSM-6490LV. X-ray diffraction (XRD) of powder and ceramics were made on the Ultima IV diffractometer in CuKα radiation (30 kV/30 mA) with a curved graphite crystal monochromator by Rigaku company (Japan) in the angular range 2θ = 10-100° in steps of 0.04° and the exposition time at point for 3 second. Processing of these measurements was conducted using the program PowderCell 2.4 for full-profile analysis of X-ray data. Analysis of the diffraction profiles and selection of true physical expansion of the peaks was performed by approximation. Separating of the effects of expansion of the diffraction peaks associated with the size of coherent scattering region (CSR), was carried out using the approach of Hall-Williamson.

3. EXPERIMENTAL RESULTS AND DISCUSSIONS

The results of X-ray investigation of powder and ceramic samples are shown in Fig.1 and Table 1. As seen all powder samples are single-phase with space groups R-3c for LSMO and Pnma for LCMO, respectively. Moreover, the phase composition of powders is identical for LSMO-0 and LSMO-2 (as for LCMO-0 and LCMO-2). Their differences are the cell volumes and CSR (or crystallite size in Tab.1) where the later for powders with x = 0 is twice more than for x = 0.2 at identical synthesis conditions. These are possible that in thin films and nanoparticles the different dopants (in our case Sr, Ca and Mn) will affect the surface enthalpy differently and, consequently, the surface electronic structure and/or surface composition [10].

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Fig. 1 – X-ray diffraction patterns of the nanopowders and high temperature ceramics with and without excess manganese for LCMO (a) and LSMO (b) manganites.

Table 1 – Phase composition and structural parameters of test samples by analysis of X-ray data.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Formula</th>
<th>Space group</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>V (Å³)</th>
<th>Crystalite size (Å)</th>
<th>Content (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Powders</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LSMO-0</td>
<td>La0.67Sr0.33MnO3</td>
<td>167: R-3c</td>
<td>5.4830</td>
<td>5.4830</td>
<td>13.358</td>
<td>347.77</td>
<td>300</td>
<td>100</td>
</tr>
<tr>
<td>LSMO-2</td>
<td>La0.67Sr0.33MnO3</td>
<td>167: R-3c</td>
<td>5.497</td>
<td>5.497</td>
<td>13.356</td>
<td>349.60</td>
<td>163</td>
<td>100</td>
</tr>
<tr>
<td>LCMO-0</td>
<td>La0.65Ca0.35MnO3</td>
<td>62: Pnma</td>
<td>5.434</td>
<td>7.686</td>
<td>5.474</td>
<td>228.59</td>
<td>244</td>
<td>100</td>
</tr>
<tr>
<td>LCMO-2</td>
<td>La0.65Ca0.35MnO3</td>
<td>62: Pnma</td>
<td>5.451</td>
<td>7.694</td>
<td>5.491</td>
<td>230.30</td>
<td>149</td>
<td>100</td>
</tr>
<tr>
<td>Ceramics</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LSMO-0</td>
<td>La0.67Sr0.33MnO3</td>
<td>167: R-3c</td>
<td>5.480</td>
<td>5.480</td>
<td>13.343</td>
<td>346.97</td>
<td>510</td>
<td>100</td>
</tr>
<tr>
<td>LSMO-2</td>
<td>La0.67Sr0.33MnO3</td>
<td>167: R-3c</td>
<td>5.520</td>
<td>5.520</td>
<td>13.386</td>
<td>352.24</td>
<td>1373</td>
<td>98</td>
</tr>
<tr>
<td>Mn3O4</td>
<td>Mn3O4</td>
<td>141: I41/amd</td>
<td>5.763</td>
<td>5.763</td>
<td>9.441</td>
<td>315.61</td>
<td>297</td>
<td>2</td>
</tr>
<tr>
<td>LCMO-0</td>
<td>La0.25Ca0.75MnO3</td>
<td>62: Pnma</td>
<td>5.472</td>
<td>7.709</td>
<td>5.452</td>
<td>230.02</td>
<td>756</td>
<td>66</td>
</tr>
<tr>
<td>LCMO-2</td>
<td>La0.25Ca0.75MnO3</td>
<td>62: Pnma</td>
<td>5.453</td>
<td>7.703</td>
<td>5.468</td>
<td>229.70</td>
<td>891</td>
<td>34</td>
</tr>
</tbody>
</table>

Furthermore, Mn will readily adopt several different valence states, unlike the alkaline earths Ca and Sr, and readily segregates to the near-surface region [13] and, consequently, the surfaces of LSMO-2 (LCMO-2) samples with excess manganese have a smaller Sr (or Ca) concentration than for the LSMO-0 and LCMO-0 that lead to obtaining of smaller size of single phase nanoparticle.

After sintering at high temperature the ceramic samples differ in the phase composition and content of its phase. The ceramic LSMO-0 has stoichiometric composition phase as distinct from the ceramic LCMO-0 consisting two phases with identical Pnma space groups and cell volumes, but with different content of dopant calcium where the stoichiometric composition is 34%. However, the other picture is observed in ceramics with excess manganese. Both samples have two phases: stoichiometric manganite and Mn3O4 hausmannite which is visible on SEM images (see Fig.2). As shown on Fig.2 LSMO-0 and LCMO-0 samples differ from LSMO-2 and LCMO-2 not only in size and shape of grains, but also internal multilayer structure of grain [8, 9]. According to X-ray data in Table 1 the values of CSR are 140 and 70 nm for LSMO-2 and LCMO-2, respectively that in good agreement with the layer size.

These substantial differences in the composition and structure of the ceramics with and without excess manganese are obviously associated with different diffusion mechanisms in these materials during sintering. As is known, additives or dopants at high sintering temperatures are diffused into the grain boundary or segregated inside the grain in a separate phase as a function of the size of dopant ion, path length to the grain boundaries, the sintering time and other [14]. Since the radii of the ions of La+3 and Ca+2 are almost equal (rLa+3 = 1.22 Å, rCa+2 = 1.18 Å, rSr+2 = 1.31 Å) [15], then Ca ion diffuses into the grain boundary much harder, however, it is quite possible its segregation inside the grain. In addition, when the temperature decreases (cooling process),...
for the same reasons the present dopants can be ununiform distributed throughout the grain body, as is observed in LCMO-0. The LCMO-2 and LSMO-2 ceramics contain an excess Mn, which released at the grain boundary already at 1200 °C [7], and at almost melting temperatures (1450-1500 °C) it leads to a change in the matter transfer mechanisms from a solid phase to a liquid-phase sintering [8,9].

4. SUMMARY

The evolution of structure of (La0.65Sr0.35)x+0.05MnO3-δ and (La0.65Ca0.35)x+0.05MnO3-δ lanthanum manganites with x = 0 and 0.2 from nanosize powder to high temperature ceramics was studied. According to X-ray investigations it is found that excess manganese isn’t integrated to a lattice of manganite because of it easily segregates to the near-surface region reducing the concentration of Ca and Sr in the surface, in consequence of that the particles size of single phase manganites with excess manganese (x = 0.2) is twice less than in manganites with x = 0 at identical synthesis conditions. Also excess manganese plays the main role in a sintering process at high temperature. Its presence leads to saving of phase composition and the forming of nanosize multilayer grain structure of ceramics.

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REFERENCES