Synthesis, structure and electrophysical properties of cation-deficient lantanium-calcium manganites

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Systems based on lantanium manganite doped with various amounts of alkali earth oxides are promising materials for cathodes in SOFC. In ideal perovskite structure the substitution of a divalent alkaline element for La^{3+} introduces Mn^{4+} ions. In real materials there is oxygen non-stoichiometry and the presence of cation vacancies that affects properties of the manganites. If concentration of defects increases, then the formation of extended defects is expected that may lead to drastic change in physical and chemical properties of the manganites.

In this work cation-deficient solid solutions $La_{0.6}Ca_{0.4}MnO_{3-z}$ systems have been synthesized. Two series of the materials have been obtained: $La_xCa_{0.4}MnO_{3-z}$ ($0 < x < 0.4$) and $La_{0.6}Ca_xMnO_{3-z}$ ($0 < x < 0.15$), deficient in La- and Ca-ions respectively. The analysis of X-ray diffraction data shows that in all systems under study solid solutions are formed with close to ideal cubic perovskite lattice. The lattice parameter monotonically changes with the defect concentration (Fig.1). It turned that the oxygen content is also monotonically decreases with the increase in the cation deficiency. (Fig.2).

Thus, the introduction of defects in A-cation sublattice of the perovskites under study results in removal of oxygen ions that facilitates the charge compensation process. It favors to the formation of extended defects. Preliminary investigations show that the cation deficient perovskites exhibits higher reactivity compared with ones with completed lattice. The work is in progress on revealing such defects and their effect on transport properties of the manganites under study.

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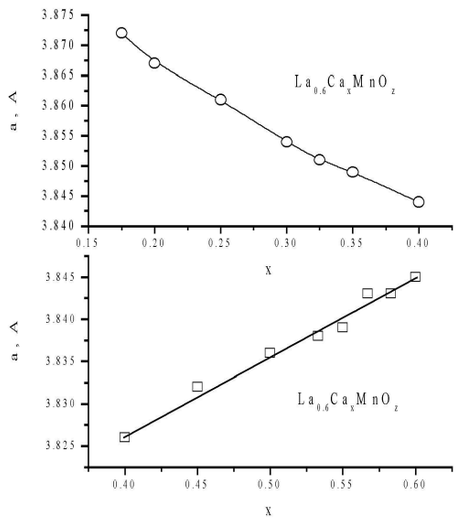

Fig.1. Dependence of the lattice parameter on composition in solid solutions $La_xCa_{0.4}MnO_{3-z}$ ($0 < x < 0.4$) and $La_{0.6}Ca_xMnO_{3-z}$ ($0 < x < 0.15$).

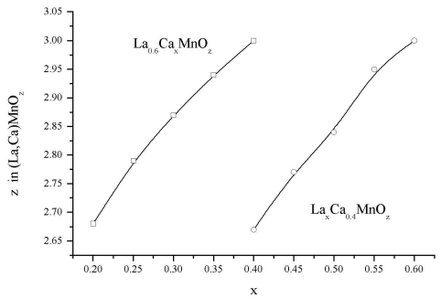

Fig.2. The dependence of the oxygen content on composition in $La_xCa_{0.4}MnO_{3-z}$ ($0 < x < 0.4$) and $La_{0.6}Ca_xMnO_{3-z}$ ($0 < x < 0.15$).