

Oxidation states of copper ions and magnetic properties of $(\text{La}_{0.7}\text{Sr}_{0.3})(\text{Mn}_{1-x}\text{Cu}_x)\text{O}_{3\pm\delta}$ system

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Lanthanum manganites, $\text{La}_{1-y}\text{A}_y\text{Mn}_{1-x}\text{B}_x\text{O}_3$ (where A is an alkali-earth metals ion, B is a 3d metals ion) are very attractive both from scientific and practical point of view as materials with colossal magnetoresistance which can be used for magnetic sensors. Partial substitution of manganese ions by copper leads to a reduction of Zener energy of the double exchange and allows controlling decrease of the 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 $[\text{Mn}^{4+}]/[\text{Mn}^{3+}]$ 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 $(\text{La}_{0.7}\text{Sr}_{0.3})(\text{Mn}_{1-x}\text{Cu}_x)\text{O}_{3-\gamma}$ system ($0 \leq x \leq 0.15$).

Bulk samples of $(\text{La}_{0.7}\text{Sr}_{0.3})(\text{Mn}_{1-x}\text{Cu}_x)\text{O}_{3-\gamma}$ 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 $\text{Mn}^{4+}\text{-O-Mn}^{3+}$ 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 ($0 \leq x \leq 0.15$), 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 $x \leq 0.05$ 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 $(\text{La}_{0.7}\text{Sr}_{0.3})(\text{Mn}_{1-x}\text{Cu}_x)\text{O}_{3-\gamma}$ system, which was verified and confirmed experimentally.