Structural and magnetic properties of nanocrystalline $La_{1-x}Sr_xMnO_{3+\delta}$

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The mixed oxides of the general formula $La_{1-x}R_xMnO_3$, where R denotes bivalent alkaline-earth constitute a large family of the manganese perovskites interesting from the fundamental as well as applications aspects, e.g. in the field of the colossal magnetoresistance [1], magnetic resonance imaging contrast agent and more recently in magnetic fluid hyperthermia [2-4]. They exhibit a large variety of properties mainly influenced by the structural distortions and manganese valency.

Recently, the influence of the oxygen stoichiometry on the structural and magnetic properties of $La_{1-x}Sr_xMnO_3$ nanoparticles in the composition range of $0 \leq x \leq 0.45$ and size of 17-30 nm was observed [5, 6]. The present work is a continuation of this investigation in the way of a better understanding of the interplay between the composition, structure and size of the particles.

Syntheses of nanocrystalline particles of the general formula $La_{1-x}Sr_xMnO_{3+\delta}$ were carried out employing sol-gel technique followed by thermal treatment at 700 °C, 800 °C and 900 °C, under flowing oxygen atmosphere. All the prepared nanocrystals were found to be rhombohedral with space group R-3c as expected.

The temperature and oxygen partial pressure applied during the synthesis of the studied materials induce deviations of the oxygen stoichiometry from the ideal one. Manganite perovskites $La_{1-x}Sr_xMnO_{3+\delta}$ are known to present either an "oxygen excess" expected for lowest temperatures and characterized by the parameter $\delta > 0$. With respect to the electroneutral condition, the actual state requires presence of cationic vacancies. Because their distribution between A and B sites is uniform as confirmed by our X-ray analysis, the original formula can be rewritten as: $La^{3+}_a Sr^{2+}_b \square_e Mn^{3+}_c Mn^{4+}_d \blacksquare_f O_3$ where $\square$ and $\blacksquare$ denote vacancies on A and B sites, respectively, and, $a = 3(1 - x)/(3 + \delta)$, $b = 3x/(3 + \delta)$, $c + d = a + b = 3/(3 + \delta)$, $e = f = 1-(a + b)$. Condition of the electroneutrality gives $3a + 2b + 3c + 4d = 6$. Therefore it is possible replace in the following part of study the term "oxygen stoichiometry" given as $(3 + \delta)$ either by the corrected stoichiometric coefficient b of Sr^{2+} ions or by the ratio $Mn^{4+}/(Mn^{4+} + Mn^{3+})$. The applied heating procedure led to an "oxygen excess" and thus to an increase of the Mn^{4+} content in comparison to the ideal stoichiometry. This deviation, associated with vacancies on A- and B-sites, is all the more pronounced since materials are lanthanum-rich, as was mentioned previously [6]. At the same time the crystallite sizes increase with heating temperature in the range of 15 nm - 100 nm.

The X-ray analysis evidences a gradual contraction of the Mn-O bond distance and consequently a decrease of the elementary cell volume when b increases or heating temperature decreases. The effect is consistent with the decrease of the mean radii $r(Mn)_B$ induced by an increase of the content of tetravalent manganese ions on manganese sites. Moreover, the evolution of Mn-O-Mn angle and rhombohedral angle that the distortion decreases when b increases or heating temperature decreases.

The magnetic behaviour of the synthesized nanoparticles depends on the compositional effects influencing magnetic interactions via $Mn^{4+}/(Mn^{3+}+Mn^{4+})$ ratio and steric distortion. The determined dependences of the magnetization and Curie temperature on the $Mn^{4+}/(Mn^{3+}+Mn^{4+})$ ratio (see Figs. 1a, 1b and 1c) thus consist of two branches separated by the maxima lying at ~ 0.4 ÷ 0.5, depending on the crystallite sizes.

Let us note that the described effects usually act simultaneously and it is difficult to separate their individual contributions. Nevertheless in spite of the encountered difficulties we attempted to show their significant influence on the evolution of the structural distortion and magnetic properties, namely magnetization and Curie temperature.

Author and coworkers believe better understanding of the interplay between the composition, structure, and size of the nanocrystalline particles of $La_{1-x}Sr_xMnO_{3+\delta}$ help their application in the field of magnetic resonance imaging and magnetic fluid hyperthermia for treatment of oncological diseases.

Acknowledgements

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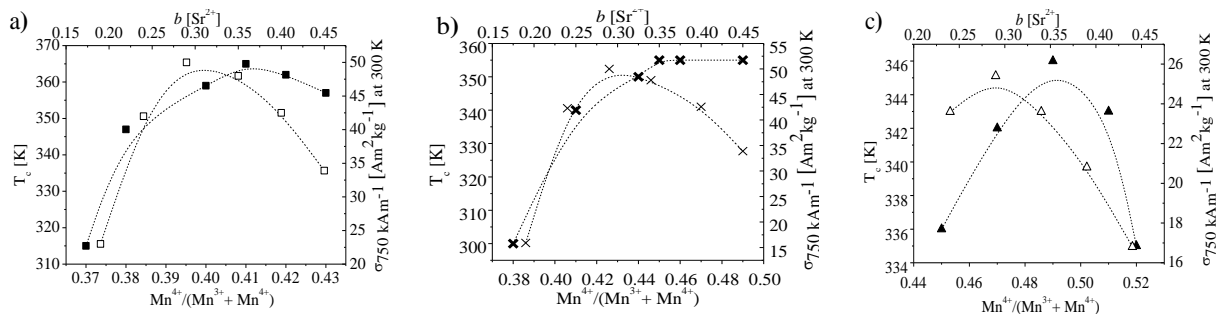
Figures

Fig. 1: Dependence of the magnetization and the Curie temperature on the relative contents of tetravalent manganese ions $Mn^{4+}/(Mn^{3+} + Mn^{4+})$ determined by chemical analysis. a) 900 °C, (■) Tc, (□) magnetization, 66 ± 15 nm; b) 800 °C, (✖) Tc, (×) magnetization, 30 ± 8 nm; c) 700 °C, (▲) Tc, (△) magnetization, 19 ± 3 nm. The connecting dashed lines are only guides for the eye.