Structural and magnetic properties of nanocrystalline lanthanum – strontium manganese perovskites

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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, like the colossal magnetoresistance [1] and more recently magnetic fluid hyperthermia [2-4]. Therefore while the previous studies were carried out mostly on the bulk materials now it is desirable to pay an attention on the magnetic nanoparticles. The present contribution is a continuation of this matter [5,6] in a specific way of an interplay between the cationic compositions, oxygen stoichiometry, structure, size of the particles and their magnetic properties.

A set of single phase nanocrystalline perovskites of the formal composition $La_{1-x}Sr_xMnO_{3+\delta}$ ($0.2 \leq x \leq 0.45$) was successfully synthesized employing sol – gel processing and annealed at 700 °C, 800 °C and 900 °C, respectively.

Let us note that for a clarity an "oxygen excess", characterized by the parameter $\delta > 0$ corresponds in reality to the cationic vacancies and "oxygen deficiency", characterized by the parameter $\delta < 0$ corresponds to the oxygen vacancies. Therefore the actual composition should be rewritten as $La^{3+}_a Sr^{2+}_b Mn^{3+}_c Mn^{4+}_d O_3$ where $a = 3(1-x)/(3+\gamma)$, $b = 3x/(3+\gamma)$ and $c + d = 3/(3+\gamma)$.

All the prepared nanocrystals were found to be rhombohedral with space group R-3c. The controlled valency mechanism, formally described as $La^{3+} + Mn^{3+} \leftrightarrow Sr^{2+} + Mn^{4+}$ together with a successive lowering of the heating temperature lead to an increase of the content of tetravalent manganese ions and a gradual decrease of the steric distortions.

Thus an interplay of both these effects provoked by the compositional changes, i.e variation of the Mn^{3+}/Mn^{4+} ratio and the bonding angles Mn-O-Mn are decisive for the resulting magnetic behaviour and one can expect three different situations concerning the magnetic interactions: ratio of $Mn^{3+}/Mn^{4+} > 1$ where the antiferromagnetic superexchange interactions Mn^{3+}_γ-O^{2-}_σ-Mn^{3+}_γ compete with ferromagnetic double exchange interactions Mn^{3+}_γ-O^{2-}_σ-$Mn^{4+}_\varepsilon \leftrightarrow Mn^{4+}_\varepsilon$-$O^{2-}_\sigma$-$Mn^{3+}_\gamma$; ratio of $Mn^{3+}/Mn^{4+} = 1$ where solely ferromagnetic phase possessing double exchange interactions Mn^{3+}_γ-O^{2-}_σ-$Mn^{4+}_\varepsilon \leftrightarrow Mn^{4+}_\varepsilon$-$O^{2-}_\sigma$-$Mn^{3+}_\gamma$ is present; ratio of $Mn^{3+}/Mn^{4+} < 1$ where the antiferromagnetic superexchange interactions Mn^{4+}_ε-O^{2-}_π-Mn^{4+}_ε compete with ferromagnetic double exchange interactions Mn^{3+}_γ-O^{2-}_σ-$Mn^{4+}_\varepsilon \leftrightarrow Mn^{4+}_\varepsilon$-$O^{2-}_\sigma$-$Mn^{3+}_\gamma$.

Further it is the size when resulting magnetic properties are influenced by a difference between the inner part of particles where spins are ordered and the outer surface layers where spins become disordered.

A simultaneous acting of these influences is documented by a comparison of the measured dependences of magnetization given in Fig. 1 and a similar behaviour exhibit the evolution of the Curie temperature.

Acknowledgements

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References

[1] Colossal magnetoresistive oxides , ed. Y. Tokura, Gordon and Breach, New York, 2000
[2] Vasseur S., Duguet E., Portier J., Goglio G., Mornet S., Hadová E., Knížek K., Maryško M., Veverka P., Pollert E., J. Magn. Magn. Mater., **302** (2006) 315
[3] Pollert E., Knížek K., Maryško M., Kašpar P., Vasseur S., Duguet E., J. Magn. Magn. Mater., **316** (2007) 122
[4] Kaman O., Pollert E., Veverka P., Veverka M., Hadová E., Grünwaldová V., Vasseur S., Epherre R., Mornet S., Goglio G., Duguet E., Nanotechnology **20** (2009) 275610 (7pp)
[5] Epherre R., Duguet E., Mornet, S., Pollert, E., Louguet S., Lecommadoux S., Schatz C., Goglio G., J.Mater. Chem. **21** (2011) 4393

[6] Epherre R., Pepin C., Penin N., Duguet E., Mornet S., Pollert E., Goglio G., J. Mater. Chem **21** (2011) 14990

Figures

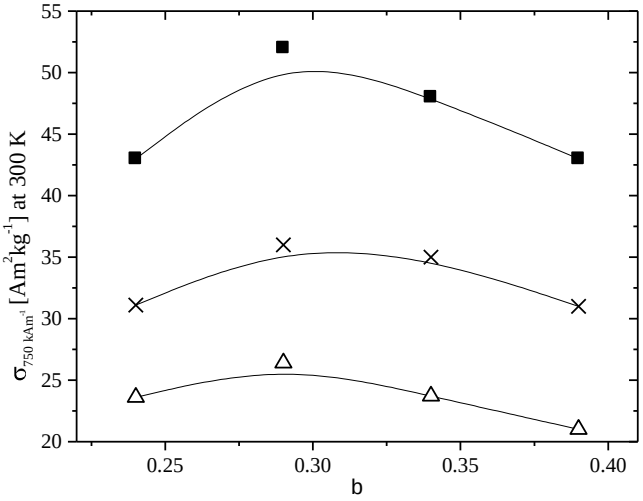

Fig. 1: Dependence of the magnetization on the composition and mean size of the magnetic cores, 66 ± 10 nm - ■ , 30 ± 5 nm – x , 19 ± 3 nm - △