Effect of electronic configuration of substituents for manganese and nonstoichiometry defects on the properties of $La_{0.7}Sr_{0.3}Mn_{0.9}{}^{57}Fe_{0.05}Me_{0.05}O_{3+\gamma}$ (Me = Zn, Mg) manganites

V. Karpasyuk,[1] A. Badelin,[1] R. Eremina,[2] S. Estemirova,[1,3,4] and F. Vagizov[5]

[1] *Astrakhan State University, 414056, Astrakhan, Russia*
[2] *Zavoisky Physical-Technical Institute, 420029, Kazan, Russia*
[3] *Institute for Metallurgy UB RAS, 620016, Yekaterinburg, Russia*
[4] *Ural Federal University, 620002, Yekaterinburg, Russia*
[5] *Kazan Federal University, 420008, Kazan, Russia*

Structural and magnetic characteristics of $La_{0.7}Sr_{0.3}Mn_{0.9}{}^{57}Fe_{0.05}Zn_{0.05}O_{3+\gamma}$ and $La_{0.7}Sr_{0.3}Mn_{0.9}{}^{57}Fe_{0.05}Mg_{0.05}O_{3+\gamma}$ manganites containing Mössbauer isotope ^{57}Fe are investigated and compared. The Zn^{2+} and Mg^{2+} ions have almost identical radii (0.74 and 0.72 Å), but different configurations of electron shells ($3d^{10}$ and $2p^6$, correspondingly). Ceramic samples were sintered in air at 1473 K. They were then exposed to heat treatments at 1223 K and partial pressure of oxygen in the gas phase of $P_{O2} = 10^{-1}$ Pa, 10^{-8} Pa, and 101.3 kPa, which ensured the production of manganites with stoichiometric oxygen content ($\gamma = 0$), with $\gamma < 0$ (containing anion vacancies) and $\gamma > 0$ (containing cation vacancies), respectively. All synthesized manganites have rhombohedral crystal structure. Mössbauer spectroscopy data correspond to Fe^{3+} ($3d^5$) ions. Non-stoichiometry index (γ) is calculated from the data on unit cell volume according to algorithm proposed earlier [1,2]. The following values of γ are obtained: γ = -0.005; 0.000; 0.007; 0.008 for Zn-containing manganites (ZnM), and γ = -0.022; 0.000; 0.002; 0.005 for Mg-containing manganites (MgM). ZnM have essentially higher values of magnetization, Curie point (T_c), and narrowest temperature interval (ΔT) of "ferromagnetic-paramagnetic" transition as compared to MgM. Their structure can be considered as more homogeneous, which corresponds to a lower value of quadrupole splitting (QS). Manganites annealed in oxygen have the narrowest ΔT, apparently due to vacancy mechanism of cation diffusion that smooths out spatial variations of the composition. Magnetization and T_c of ZnM increase in general with increasing the oxygen content, showing a plateau in the intermediate range of γ. MgM have similar dependence of T_c on γ, but their magnetization has a maximum at $\gamma = 0$ and a sharp decline at $\gamma = 0.005$, although QS at latter point is minimal. The results obtained indicate that different effect of Zn^{2+} and Mg^{2+} ions on electromagnetic characteristics of manganites is largely determined by the configuration of their electron shells.

References:

[1] V.K. Karpasyuk, A.G. Badelin, D.I. Merkulov, I.M. Derzhavin, S.Kh. Estemirova, J. Phys.: Conf. Ser. **1347**, 012036 (2019).
[2] D. Merkulov, A. Badelin, S. Estemirova, V. Karpasyuk, Acta Phys. Pol. A **127**, 248 (2015).

This work was supported by the Russian Foundation for Basic Research (grant no. 18-52-06011)