

Nanocomposites and nanomaterials

Excess manganese as a stabilization factor of the phase composition of nanoscale manganites

A.O. Novokhatska, G.Ya. Akimov

*Donetsk Institute for Physics and Engineering named after O.O.Galkin, Natl. Acad. of Sci. of Ukraine. Prospect Nauki, 46, Kiev-03039, Ukraine.
E-mail: a.novokhatska@gmail.com*

Cation segregation at the surface and the interfaces of transition-metal oxides impacts the reactions that are often critical to the overall device performance in a range of device applications. In particular, cation segregation on perovskite oxide surfaces impacts tremendously the reactivity and stability of solid oxide fuel cell (SOFC) cathodes. According to [1], in the $\text{La}_{0.65}\text{A}_{0.35}\text{MnO}_3$ ($\text{A} = \text{Ca}, \text{Sr}, \text{Ba}$) compositions, the completing layer is oxide Mn-O , and the doped cations A segregate into a surface layer as temperature increases, which decreases their concentration in the volume of the material. In addition, a large mismatch between radii of the rare-earth and alloying ions is also the moving force of their drift to the surface.

In this work, we present the results of studies of the influence of excess manganese on the formation of the properties of nanosize manganite powders of $(\text{Nd}_{0.67}\text{Sr}_{0.33})_{1-x}\text{Mn}_{1+x}\text{O}_3$ ($x=0, 0.2$) that were used for preparing of SOFC cathodes. According to the research results [2] the introduction of excess manganese ($x=0.2$) into the batch allows to obtain in the synthesis process a single phase material with a crystallite size of two times less than in manganites with $x=0$. It is shown that Mn^{2+} ion have large mismatch between the radii of doping cations and Nd^{3+} ion; moreover, Mn can be in several various valence states. Therefore, the excess Mn can much easier drift into the surface layer than other doped cations. This drift of excess Mn made it possible to decrease the excess surface energy and to balance the charge state on the surface, which leads to balancing of the whole system at nanoscale of crystallite. The excess manganese remained on the crystallite surface and played a very important role during sintering in the formation of the structure and the conductive properties of manganite cathode ceramics.

1. Wonyoung Lee, Jeong Woo Han, Yan Chen, Zhuhua Cai, and Bilge Yildiz. Cation Size Mismatch and Charge Interactions Drive Dopant Segregation at the Surfaces of Manganite Perovskites // Journal of American Chemical Society. -2013.- **135**,-P. 7909 –7925.
2. G. Ya. Akimov and A. A. Novokhatska. Role of excess manganese in the formation of properties of nanometer-sized manganite powders// Physics of the Solid State. – 2016. - **58**, - P. 1213–1215.