

IN SITU AND EX SITU STUDY OF CUBIC $\text{La}_{0.5}\text{Ba}_{0.5}\text{CoO}_{3-\delta}$ TO DOUBLE PEROVSKITE $\text{LaBaCo}_2\text{O}_{6-\delta}$ TRANSITION

Dmitry Malyshkin, Institute of Natural Sciences and Mathematics, Ural Federal University, Yekaterinburg, Russia
Dmitry.Malyshkin@urfu.ru

Andrey Novikov, Institute of Natural Sciences and Mathematics, Ural Federal University, Yekaterinburg, Russia

Anton Sednev, Institute of Natural Sciences and Mathematics, Ural Federal University, Yekaterinburg, Russia

Vladimir Sereda, Institute of Natural Sciences and Mathematics, Ural Federal University, Yekaterinburg, Russia

Ivan Ivanov, Institute of Natural Sciences and Mathematics, Ural Federal University, Yekaterinburg, Russia

Dmitry Tsvetkov, Institute of Natural Sciences and Mathematics, Ural Federal University, Yekaterinburg, Russia

Andrey Zuev, Institute of Natural Sciences and Mathematics, Ural Federal University, Yekaterinburg, Russia

Key Words: Double perovskites, Disordered–ordered transition, Domain textured phases, Equilibrium phase diagram.

Double perovskites $\text{REBaCo}_2\text{O}_{6-\delta}$ (RE – rare-earth element) have received great attention in past decades as promising materials for various electrochemical devices because of their high mixed ionic-electronic conductivity and catalytic activity for the reaction of oxygen reduction. Among these compounds, cobaltite $\text{LaBaCo}_2\text{O}_{6-\delta}$ can serve as a good example of structural flexibility, since it is able to form either A-site disordered cubic “simple” perovskite or layered A-site ordered double perovskite. However, the exact limits of the thermodynamic stability of $\text{LaBaCo}_2\text{O}_{6-\delta}$ double perovskite with respect to temperature (T) and oxygen partial pressure ($p\text{O}_2$) have not been determined so far. Furthermore, synthesis and study of selected properties of either cubic or layered $\text{LaBaCo}_2\text{O}_{6-\delta}$ oxide were mostly of interest for researchers, whereas the transition from “simple” to double perovskite was not addressed in detail so far. At the same time, it is generally recognized that such transition significantly improves oxide ion transport in the perovskite-type oxides and, therefore, understanding this order-disorder transition is of key importance for successful development of new materials for practical application.

Therefore, the present work aims at providing some insights into the nature of the aforementioned order-disorder transformation of $\text{LaBaCo}_2\text{O}_{6-\delta}$, as well as into thermodynamic stability of both ordered and disordered phases, using a set of complementary techniques such as transmission electron microscopy, *in situ* X-ray diffraction and solid state coulometric titration.

As a result, formation of complex domain textured intermediate products during the phase transition “ordered $\text{LaBaCo}_2\text{O}_{6-\delta}$ – disordered $\text{La}_{0.5}\text{Ba}_{0.5}\text{CoO}_{3-\delta}$ ” was revealed. These products were found to exhibit strong affinity to oxygen and fast oxygen exchange with ambient atmosphere even at temperature as low as 70 °C. This particularity seems to provide a unique possibility to develop a new class of advanced materials for IT SOFCs, ceramic membranes and catalysis.

The thermodynamic stability limits of the cubic and double perovskites were determined as $\log(p\text{O}_2) = f(1/T)$ dependencies. The stability diagram of the $\text{LaBaCo}_2\text{O}_{6-\delta}$ – $\text{La}_{0.5}\text{Ba}_{0.5}\text{CoO}_{3-\delta}$ system was plotted as a result. Oxygen nonstoichiometry of the thermodynamically stable cubic perovskite $\text{La}_{0.5}\text{Ba}_{0.5}\text{CoO}_{3-\delta}$ was measured as a function of $p\text{O}_2$ in temperature range between 1000 and 1100 °C using coulometric titration technique.

Acknowledgement: This study was supported by the Russian Foundation for Basic Research (Grant No. 18-33-20243).