

Effect of crystal orientation on the aliovalent dopant segregation at the surface of $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_3$

Fatih Pişkin^{1,2}, Roland Bliem² and Bilge Yildiz^{2,3}

¹Dept. of Metallurgical and Materials Engineering, Middle East Technical University, Ankara, Turkey

²Dept. of Nuclear Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, USA

³Dept. of Material Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, USA

Perovskite-type oxides with mixed electronic and ionic conductivity (MIEC) have been studied extensively due to their wide range of applications in oxygen permeation membranes, solid oxide electrolysis cells (SOECs) and solid oxide fuel cells (SOFCs). The state-of-the-art cathodes, such as the La-based transition metal perovskites (La,Sr)CoO₃ (LSC), (La,Sr)FeO₃ (LSF), and (La,Sr)MnO₃ (LSM) are attractive due to their high oxygen reduction activity and high oxygen ionic conductivity. However, most MIEC materials belonging to the ABO₃ perovskite family exhibit surface cation segregation under operating conditions. This process can be driven by strain and the electrostatic attraction of aliovalent dopants by surface oxygen vacancies [1]. The dopant segregation towards the oxide surface often leads to the formation of insulating phases that block the electron transfer and oxygen exchange pathways on the cathode surface and thus it hinders the oxygen reduction reaction. This segregation behavior is expected to depend on the surface energy, affected by the atomic arrangements of the perovskite surface [2], and thus, the crystal orientation of the oxide surface might play a key role on the dopant segregation tendency.

The current study systematically investigates the crystal orientation effect on the dopant segregation behavior of LSC with complementary surface-sensitive analytical techniques. A polycrystalline LSC pellet was produced and then annealed at 800 °C in air for several hours (2h, 5h and 10h) to induce the surface cation segregation. The correlation between the crystal orientation and the segregation tendency was investigated via scanning electron microscopy (SEM) and electron backscatter diffraction (EBSD) techniques. In this respect, the formation of segregated particles on the grains were examined in terms of both the number of particles and the respective area coverage. In the analysis, 120x140 μm² surface area, having approximately 200 grains, was investigated grain by grain to examine the segregated particles on the surface and then the orientation of each grain was confirmed by EBSD.

The results show statistically that the orientations close to <001> are more prone to cation segregation than the orientations close to <101> and <111>. The distribution of the area coverage fraction of the three main crystallographic orientations is given Figure 1. This orientation dependency indicates that the exposed facet has a significant impact on the

cation segregation. The LSC surfaces were also investigated with X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES) before and after annealing procedures to reveal the chemical state and the electrical structure of the segregated particles for each condition.

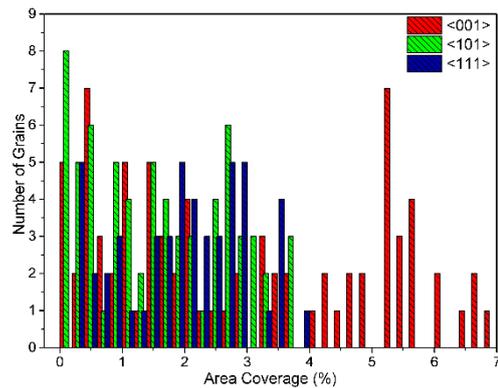


Figure 1. The histogram illustrating the number of grains exhibiting a certain area coverage of segregated particles for different crystallographic orientations.

The present study provides insights into the importance of the atomic arrangements on the surface stability and the cation segregation tendency of LSC cathode material.

References

- [1] Lee, W. et al. Cation Size Mismatch and Charge Interactions Drive Dopant Segregation at the Surfaces of Manganite Perovskites. *Journal of the American Chemical Society*, 135, 7909-7925 (2013)
- [2] Daisuke, M. et al. Synthesis, structure, and electrochemical properties of epitaxial perovskite $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_3$ film on YSZ substrate. *Solid State Ionics*, 177, 535-540 (2006)

Acknowledgements

Authors acknowledge support from the US Airforce Office of Scientific Research. F. Pişkin was supported by the TUBITAK 2214-A International Doctoral Research Fellowship Programme, No. 1059B141501191, which the authors gratefully acknowledge.



Fatih Pişkin

Fatih Pişkin is a Research Assistant in Department of Metallurgical and Materials Engineering, Middle East Technical University. He is currently Ph.D. candidate in the same department. He received his BS degree from Anadolu University in 2009, and MS degree from Middle East Technical University in 2013.

Corresponding author: Fatih Pişkin, e-mail: fpiskin@metu.edu.tr tel: +90 312 210 59 19