Investigating structure transformations of $La_xSr_{2-x}MnO_{4-\delta}$ using *in situ* 3D electron diffraction in a gas environment

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Ruddlesden-Popper manganites $La_xSr_{2-x}MnO_{4-\delta}$ recently gained interest as promising electrode materials for solid oxid fuels cells. For $0.25 \leq x \leq 0.6$, their stability under reducing atmosphere –along with the preservation of their K_2NiF_4-type I4/mmm symmetry – has been demonstrated using *in situ* high-temperature neutron and X-ray powder diffraction. [1] However, abnormally large anisotropic displacement parameters and complex changes in cell parameters point to the presence of disorder, which might explain the material's increased electrical conductivity in diluted hydrogen. Submicron sized crystals are sufficient for electron diffraction (ED) to obtain two-dimensional single-crystal diffraction patterns, which can be interpreted in a more straightforward way than powder data. Therefore, single-crystal ED might pick up features which were missed during X-ray and powder diffraction. Using a dedicated environmental holder in a transmission electron microscope, we performed several series of *in situ* ED experiments to track structure transformations of $La_{0.5}Sr_{1.5}MnO_4$ upon heating in a 5% H_2 /He atmosphere. As the current state-of-the-art *in situ* equipment only permits tilting of the holder along one axis, conventional in-zone patterns cannot be obtained, and 3D ED is the optimal method to acquire sufficient diffraction data for structure analysis. We also performed the same experiments on Sr_2MnO_4 as a reference, since this material is known to undergo a space group transformation to a monoclinic $P2_1/c$ supercell when reduced to $Sr_2MnO_{3.55}$ [2]. For $La_{0.5}Sr_{1.5}MnO_4$ a coexistence of both the tetragonal Ruddlesden-Popper phase and a perovskite phase has been noted upon heating to 750°C in reducing atmosphere, which has not been reported before. However, apart from the diluted hydrogen, the electron beam might possess some reductive power too, and the high temperatures can lead to decomposition. Therefore, we systematically examined the influence of different external factors, repeating the experiment with i.a. varying beam exposures, while heating in vacuum and reducing *ex situ* in 5% H_2 /He.

[1] Sandoval, M., Pirovano C., Capoen, E., Jooris, R., Porcher, F., Roussel, P., Gauthier, G. (2017). *Int. J. Hydrog. Energy.* **42 (34),** 21930-21943.

[2] Broux, T., Bahout, M., Hernandez, O., Tonus, F., Paofai, S., Hansen, T., Greaves, C. (2013). *Inorg..Chem.* **52 (2)**, 1009-1017.

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