Uncovering hidden complexity in oxygen deficient perovskites

M. Batuk, D. Vandemeulebroucke, J. Hadermann

EMAT,University of Antwerp, Belgium

joke.hadermann@uantwerpen.be

Oxygen deficient perovskites are investigated as oxygen carriers for many different energy applications, based on the possibility to change their oxygen content while maintaining the cation framework. The most well-known oxygen deficient perovskite type structure is brownmillerite, with alternating layers of octahedra and tetrahedra. However, even for this common structure there are complexities such as ordered rotations of tetrahedra that are often missed during structure determination using, for example, powder diffraction, resulting in the persistent use in literature of inaccurate structure models for DFT calculations and properties explanations. When the extra reflections corresponding to the anion related order are picked up in single crystal neutron or X-ray diffraction, the refinement is often still hindered by high amounts of twinning or correlated disorder. In such cases, TEM can shed a light on the structure, in the past through mostly qualitative techniques like high resolution imaging of the structure and visualization of the reflections using electron diffraction, nowadays also through refinement of the structure from single crystal 3DED data. Electron diffraction is more sensitive to low Z atoms such as oxygen next to heavier atoms than X-rays and can be used on submicron sized crystals; the problems there once were with dynamical scattering are overcome using 3DED [1] combined with dynamical refinement [2]. Using TEM, compounds that were commonly accepted to be brownmillerites were proven to have a completely different anion deficient perovskite type structure, for example $Pb_2Fe_2O_5$ [3] and related compounds, "disordered" brownmillerites like $Sr_2Fe_2O_5$ [4] and $Sr_2Co_2O_5$ [5] were shown be ordered, and clear oxygen-vacancy order that escaped characterization with other techniques was found in many oxygen deficient perovskites, such as in $LaSrCuO_{3.5}$ [6] and $SrMnO_{3.5}$ [7]. So far, such crystal structures were derived in TEM experiments after reduction outside the microscope, however, the results of the first in situ 3DED redox experiments will also be shown, which allow to follow the structure evolution between oxygen deficient and oxidized perovskite by acquiring in situ 3DED data on submicron sized single crystals in different oxidizing and reducing gasses. In short, I will show that there might be more complexity underlying still many published structures, which we are now better equipped to uncover using electron crystallography, no longer only by observing the superstructures but now also by quantifying them, reliably refining the structures and taking control of the oxygen content during the TEM experiments themselves.

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