Determination of local structure and bonding in nanoscale oxides by electron energy-loss spectroscopy

Stuart Turner[1], Maria Meledina[1], Ying-gang Lu[1], Nicolas Gauquelin[1], Johan Verbeeck[1], Gustaaf Van Tendeloo[1]

[1] EMAT, University of Antwerp
Groenenborgerlaan 171 – B-2020 – Antwerp - Belgium. Email: stuart.turner@uantwerp.be

In nanoscale metal oxides, bonding and electronic structure of the metal cations are of fundamental importance for the electronic, magnetic, catalytic and ionic transport properties of the material. On top of bulk materials properties, local structural or coordination/valency changes can be key factors in many materials applications. For example, cation valency changes at the final terminating surface planes can be important for many catalytic processes, while changes in cation coordination or valency at defects like twin boundaries, grain boundaries and interfaces can greatly affect the electronic, optical and transport properties of bulk materials and thin films. Being able to measure changes in valency and oxygen coordination at atomic resolution is therefore a major challenge in oxide materials, whether in the form of bulk material, thin films, nanowires or particles.

Atomic resolution elemental mapping has become increasingly feasible over the past years by means of spatially resolved electron energy-loss spectroscopy (EELS) and energy dispersive X-ray spectroscopy in a scanning transmission electron microscope (STEM-EELS and STEM-EDX). Recent improvements in microscope instrumentation like high-brightness electron sources, aberration correctors, electron monochromators and state-of-the-art X-ray and EELS spectrometers allow atomic resolution fine structure investigation to be performed with energy resolutions below 100 meV and at atomic spatial resolution. This means that intricate details in the EELS edge fine structure, linked to e.g. the coordination or valency of transition metals cations, can be investigated [1, 2].

In this contribution, results on local structure and bonding determination in nanoscale oxides through investigation of the energy-loss near-edge structure (ELNES) will be presented. Proof-of-principle experiments, like Fe coordination mapping in $Pb_2Sr_2Bi_2Fe_6O_{16}$ (Figure 1) [3], will be discussed together with applications in catalysis (Fe-doped ceria nanoparticles for chemical looping) and optics (epitaxially grown ITO nanowires) [4].

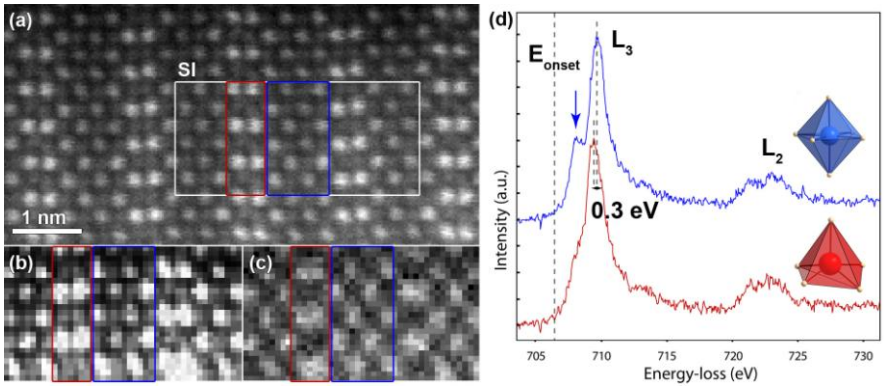

Fig.1 Site-specific Fe $L_{2,3}$ ELNES investigation of a $Pb_2Sr_2Bi_2Fe_6O_{16}$ complex oxide (a) HAADF-STEM overview image along the [010] zone axis orientation, showing 5-fold coordinated Fe regions (red) and 6-fold coordinated Fe regions (blue)in the acquired spectrum-image region (white rectangle) (b) SI HAADF signal (c) Fe map, showing the B-cation (Fe) positions. (d) Summed Fe $L_{2,3}$ edges from the 6-fold coordinated Fe sites (blue spectrum, blue region indicated in in (b) and (c)) and 5-fold coordinated Fe sites (red spectrum, red region indicated in (b) and (c)). Different oxygen coordination of the Fe cations can be determined at atomic resolution from the acquired EELS data.

References

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