Direct Evidence of Fe^{2+}/Fe^{3+} Charge Ordering Mechanisms in Ferrimagnetic $Fe_{1.35}Ti_{0.65}O_{3-\delta}$ Thin Films

Laura Bocher[1], Alexandre Gloter[1], Katia March[1], E. Popova[2], M. Nolan[3], Bénédicte Warot-Fonrose[4], Niels Keller[2], Yves Dumont[2] et Odile Stéphan[1]

[1] Laboratoire de Physique des Solides - Université Paris-Sud, Groupe STEM, Bât. 510 - Orsay - France. Email: laura.bocher@u-psud.fr
[2] Groupe d'Etudes de la Matière Condensée - Université Versailles St Quentin en Yvelines, Versailles - France.
[3] Tyndall National Institute – University College Cork, Lee Maltings - Cork – Ireland
[4] Centre d'Elaboration de Matériaux et d'Etudes Structurales Toulouse - France.

Latest breakthroughs in electron spectro-microscopy techniques have paved the way toward localizing single atom positions and acquiring two-dimensional elemental maps at sub-angström resolution over large unit cells. High-energy resolution electron energy-loss spectroscopy (EELS) can probe the local bonding environment and the electronic structure of nanostructured systems.

In transition metal oxides, the $L_{2,3}$ transition metal near-edge structures present, in particular, a strong sensitivity to the valence state modulations. Combining this information with imaging capabilities in an aberration-corrected Scanning Transmission Electron Microscope (STEM), it gives us a direct access to the valence state mapping down to the atomic columns.

Hence we recently revealed direct experimental evidence of Fe^{2+}/Fe^{3+} charge ordering in hematite-ilmenite $Fe_{1.35}Ti_{0.65}O_{3-d}$ thin films using this real-space technique. The local Fe valence state distributions highlight a strong Fe^{2+} modulation correlated with a significant presence of oxygen vacancies. The magnetic and transport properties of these films are reviewed in the light of the charge ordering mechanism [1].

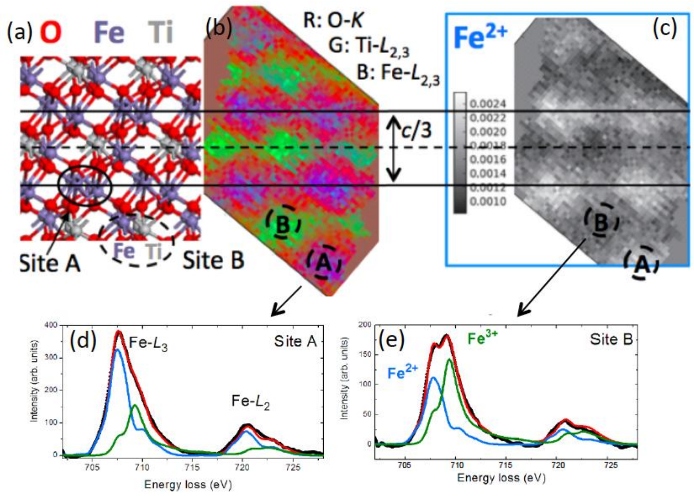

Fig. (a) $Fe_{1.5}Ti_{0.5}O_3$ structural model system, (b) reconstructed elemental map combining the O-K, Ti-$L_{2,3}$, and Fe-$L_{2,3}$ edges (red, green, and blue), and (c) and the corresponding map of the Fe^{2+} spectral weight, (d) and (e) examples of Fe-$L_{2,3}$ fine structures probed at different atomic sites.

The authors gratefully acknowledge financial support from the french CNRS (FR3507) and CEAMETSA network (www.metsa.fr). The research leading to these results has received funding from the European Union Seventh Framework Programme under Grant Agreement 312483-ESTEEM2 (Integrated Infrastructure Initiative-I3).

Références

L. Bocher, E. Popova, M. Nolan, A. Gloter, E. Chikoidze, K. March, B. Warot-Fonrose, B. Berini, O. Stéphan, N. Keller, and Y. Dumont. Phys. Rev. Lett. **111** (2013) 167202