Direct evidence of Fe$^{2+}$/Fe$^{3+}$ charge order in the ferrimagnetic hematite-ilmenite Fe$_{1.5}$Ti$_{0.5}$O$_{3-δ}$ solid solution

L Bocher$^1$, K March$^1$, A Gloter$^1$, B Warot-Fonrose$^2$, E Popova$^3$, Y Dumont$^3$, and O Stéphan$^1$

1. Laboratoire de Physique des Solides, Groupe STEM, Orsay - France
2. Centre d'Elaborations et d'Etudes Structurales, CEMES, Toulouse - France.

Email. laura.bocher@u-psud.fr
Keywords: Elemental map - Atomically-resolved ELNES – Cationic and charge orders

A strong interplay between charge, lattice, orbital and spin degrees of freedom exists in transition-metal oxides yielding the emergence of a large spectrum of functionalities such as high-temperature superconductivity, metal/insulator transition, multiferroicity, thermoelectricity... More specifically, mixed valence states of 3d elements issue as a driving force in such interplay. In addition, valence state modulations can also originate from the oxygen content variation. Recently, new physical effects were revealed at the interfaces of complex transition-metal oxides demonstrating how a precise knowledge of the atomic and electronic structures at the atomic scale becomes a pivotal point to understand better the observed physical properties at the macroscopic scale (see e.g. [1] and [2]).

Today modern technological breakthroughs in electron microscopy and spectroscopy pave the way toward (i) localizing atom positions at the sub-Angström resolution, (ii) obtaining 2D elemental maps and (iii) mapping the electronic structure at the atomic scale. For instance, studies of $L_{2,3}$ transition metal fine structures by Electron Energy-Loss Spectroscopy (EELS) can now yield direct valence state quantification at such a sub-Angström resolution. Very recently, Tan et al. successfully mapped for the first time the Mn$^{2+}$/Mn$^{3+}$ order in Mn$_3$O$_4$ at the atomic scale [3]. This proof of concept opens new perspectives to understand deeper the structure-properties relationship in complex transition-metal oxides.

Here we study a solid solution based on titanohematite (Fe$_{2-x}$Ti$_x$O$_3$), which presents interests in (i) geomagnetism as a responsible for the observed earth remanent magnetism based on the atomic scale spinodal decomposition inducing coherent interfaces between Fe$_2$O$_3$/FeTiO$_3$ exsolution lamellae [4, 5] and (ii) as a potential spintronic material as predicted by theoretical ab initio spin-resolved density of states calculations [6]. All these works have stimulated several studies on the microstructure of mineral rocks as well as the controlled elaboration of epitaxial thin films at the atomic scale [7]. However no evidence for cationic and charge orders at the atomic scale in these phases has been provided yet.

Using a new-generation of aberration-corrected scanning transmission electron microscope, the NION UltraSTEM200, we imaged and mapped the atomic structure of Fe$_{1.5}$Ti$_{0.5}$O$_3$ demonstrating a cationic order by means of the signature of a clear anti-correlation between pure Fe and mixed Fe/Ti plans over few unit cells (Fig. 1). More interestingly, relying on high-energy resolution EELS measurements on the Fe-L$_3$ edge, we provide the direct evidence of a possible Fe$^{2+}$/Fe$^{3+}$ charge ordering. This is exemplified in Figure 2 where atomically-resolved Fe, Ti, Fe$^{2+}$ and Fe$^{3+}$ maps are displayed. Linear combinations of Fe$^{2+}$ (siderite) – Fe$^{3+}$ (hematite) ELNES reference spectra were used to fit each experimental spectrum leading to the Fe$^{2+}$ and Fe$^{3+}$ reconstructed maps.

References

The authors gratefully acknowledge the METSA network for supporting this collaborative project.

**Figure 1.** a) structural model of Fe$_{1.5}$Ti$_{0.5}$O$_3$, b) atomically-resolved HAADF image and the simulated image (inset), and c) the corresponding reconstructed false color elemental maps associated with Fe-L$_{2,3}$/Ti-L$_{2,3}$ edge intensities (blue/yellow).

**Figure 2.** a) STEM-HAADF image of Fe$_{1.5}$Ti$_{0.5}$O$_{3-x}$, b) STEM-HAADF map of the scanned area for EELS acquisition, c) and d) Fe-L$_{2,3}$ and Ti-L$_{2,3}$ elemental maps respectively, e) and f) Fe$^{2+}$ and Fe$^{3+}$ reconstructed maps, respectively, and g) experimental ELNES Fe-L$_3$ fine structures extracted from pure Fe (blue) or mixed Fe/Ti (yellow) columns and the corresponding Fe$^{2+}$/Fe$^{3+}$ (green/red) ELNES Fe-L$_3$ edges of reference spectra.