Oxidation States of Mn and Fe in (Ba, Fe)-Manganite

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The properties of Ba-hexaferrites can be tailored by partially substituting Fe by other 3d transition metals. In the present work, the oxidation states of Mn and Fe in (Ba,Fe) manganites are investigated. Several techniques have been proposed to correlate EELS/ELNES features with the valence state. It is well established that the absolute energy shift, the normalized total intensity, and the ratio of white lines in EELS from transition metal oxides vary with their oxidation states [e.g. 1, 2].

The effects of oxidation state on ionization edge threshold energy and L$_{2,3}$ white line intensity ratios for Fe- and Mn-oxides are revised. Transition metal compounds of known oxidation states were used to establish calibration curves of L$_3$/L$_2$ intensity ratio vs. 3d occupancy (Mn$^{2+}$Cl$_2$, Mn$^{2+}$, Mn$^{3+}$, Mn$^{4+}$-oxides; Fe$^{2+}$, Fe$^{3+}$-oxides). To isolate the white line intensities, the background beneath the edge (fitted by A·$E^{-n}$) and the intensity due to transitions into the continuum have to be subtracted from the experimental spectra. Three continuum model functions were tested: (i) Hartree-Slater (HS), (ii) simple hydrogenic edge shape functions, and (iii) a modified power-law bkgd model (Afit; ref.[3]) fitted in two post-edge windows and extrapolated into the threshold region. Models (ii) and (iii) were modified into double steps in analogy to the HS model with step onsets at peak maxima and step height ratio 2:1. The intensity of the continuum model functions were normalized to the experimental spectra within a 2 eV energy window positioned at the relative minimum between L$_2$ and the first EXELFS oscillation; total intensities were integrated over 8 eV windows centred on the peak maxima, as shown for example in Fig.1 (MnO$_2$ reference material). Preliminary results indicate that Mn in (Ba, Fe) manganite (nominally Ba$_{Fe_8}Mn_4$O$_{19}$) is essentially in the Mn$^{4+}$ oxidation state, and the ratio Fe$^{3+}$/ΣFe > 0.5 in this compound; implications on the structure of (Ba, Fe) manganite will be discussed.

![MnO2-3b.LPdecon.sansBkgd](image)

Fig.1: Mn-L$_{2,3}$ edges in MnO$_2$; normalized Hartree Slater and Hydrogenic continuum model functions are indicated.

References