Detecting Structural and Bonding Changes in EELS Near-Edge Structures with a Monochromated TEM

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The enhanced energy resolution in electron energy loss spectroscopy measurements achieved in transmission electron microscopes equipped with monochromators provides new opportunities for the study of the properties of materials and their defects with an unprecedented spatial resolution. The current systems offering an energy resolution comparable to the one of soft x-ray absorption spectroscopy (about 0.1eV) make it possible to increase the sensitivity to changes in the near-edge structure while maintaining the capability to study small objects with a probe size better than 2nm[1]. With this improved performance, it is therefore possible to study changes in the electron energy loss spectra due to modifications of the structure or the bonding of the sample with minimal contributions due to the poor energy resolution of the instrument. This capability is a necessity for the study of transition metal oxides, and in particular compounds with perovskite-related structures, where subtle changes in the atomic arrangement or distortions in the bond angles can lead to dramatic changes in the physical properties. These structural and bonding effects are studied here by probing the variations of the O-K and Ti-L23 edges in a series of transition metal oxides.

Experiments were carried out on a FEI Tecnai-200FEG equipped with a monochromator[1] and a high-resolution electron energy loss spectrometer[2]. The first applications on a broad range of materials (including oxides, nitrides and fullerenes) and details of the performance of the system have been described elsewhere[3-5] and show that an energy resolution of about 0.1eV can be achieved yielding additional information on the near-edge structure spectra.

The O-K edge in TiO2-brookite (figure 1a) shows two well-resolved peaks attributed to the O2p hybridization with the Ti3d states that are split into t2g-eg components due to the octahedral crystal field. Experiments with and without the monochromator[3,4] supported by calculations make it possible to deduce that the width of these peaks is intrinsic to the electronic structure of this material and is due to dispersion of the hybridized states and the strong distortions of the octahedra. In the perovskite structures such as CaTiO3 and SrTiO3 (figure 1b and ref. [6]), however, the t2g peak (at 531eV) is significantly narrower and the eg peak intensity (at 533-534 eV) is significantly reduced due to the lower distortion of the octahedral environment around the cations. This sensitivity to bonding changes can be exploited when studying the variations of the local electronic structure due to substitutions of cations in perovskites. These effects can be probed in the Ba(Ti,Ru)O3 compound where some of the Ti atoms are substituted by Ru. The main features of the O-K edge of the perovskite spectra are maintained in Ba(Ti,Ru)O3 (figure 2a) since there are general similarities with the spectra of CaTiO3 (figure 1b) and BaTiO3. Differences exist, however, in the intensity of the t2g and eg peaks suggesting that strong hybrids between the Ru4d and the O2p states are also formed while the distortion of the octahedra around the Ti and Ru atoms are comparable to the ones present in BaTiO3 and CaTiO3. This effect is also supported by the fact that no major differences are observed in the general structure of the Ti-L23 edges since strong similarities also exist with the spectra of CaTiO3 (Figure 2b) and BaTiO3[7]. Further bonding effects in perovskites and in organic materials will be presented and comparisons with XAS measurements will be discussed[8].
References
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Figure 1a) O-K edge in TiO$_2$ (brookite)
Figure 1b) O-K edge in CaTiO$_3$

Figure 2a) O-K edge in Ba(Ti,Ru)O$_3$
Figure 2b) Ti-L$_{23}$ edge in CaTiO$_3$