

## Probing the Metal-Insulator Transitions in Complex Oxides with EELS Near-Edge Structures

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Electron energy loss near-edge structures (ELNES) are presently used in many materials science applications to characterize the chemical state of elements present in a broad range of samples. For example, the initial work on reference materials is now finding applications to real-life systems related to the characterization of corrosion or oxidation in engineering materials. The high spatial resolution capability of energy loss fine structure have also given new insight into the bonding mechanisms at grain boundaries and interfaces. More recently, with the help of electronic structure calculations, additional information on the bonding mechanisms in solids can be deduced and related to variations in spectra at interfaces or grain boundaries. With respect to x-ray absorption spectroscopy, however, ELNES applications to the study of electronic effects in complex oxides have been very limited. With more efficient energy loss spectrometers becoming available in interdisciplinary microscopy facilities and with the present developments in high-resolution electron energy-loss spectroscopy, ELNES will find novel applications in the study of systems with strong electronic correlations. This abstract outlines features present in the O K and Ti L<sub>23</sub> edges in the vacancy doped Nd<sub>1-x</sub>TiO<sub>3</sub> system and discussed the evolution of these features as a composition is changed and the system evolves from an insulating to a metallic state.

A detailed structural and physical characterization of the Nd<sub>1-x</sub>TiO<sub>3</sub> <sup>(1)</sup> shows that the system evolves from an anti-ferromagnetic Mott-Hubbard insulator state with p-type semiconducting behaviour (in the range of compositions x=0 to about x=0.08) to a Fermi liquid metallic behaviour (in the range x=.10 to x=.20). Further transitions to a charge transfer insulator with n-type behaviour are observed at lower Nd concentrations. In addition to these electrical properties, structural measurements have shows that the bridging Ti-O-Ti bond angle of corner shared octahedra is about 150°. EELS measurements were carried out on a CM20FEG system equipped with a GIF spectrometer. For this work, an energy resolution of 0.75-0.8eV was achieved on the system. Samples were prepared by dispersing a crushed powder of the sample on a holey C film.

In the Nd<sub>0.95</sub>TiO<sub>3</sub> sample, the O K edge reveals a small shoulder on the low energy side of the main peak (fig. 1a) that becomes fully resolved and visible as a pre-peak in the O K edge in the Nd<sub>0.88</sub>TiO<sub>3</sub> sample (Fig. 1b). In transition metal oxides, this pre-peak is normally attributed to O 2p-TM3d hybridization and the evolution with composition therefore suggests that the Fermi level moves within this energy band. Similar effects are observed as a function of oxygen content in YBCO as the O K edge pre-peak is directly related to the O content in the superconducting material. With respect to simple systems such rutile, the TiL<sub>23</sub> edges in Nd<sub>0.88</sub>TiO<sub>3</sub> and Nd<sub>0.95</sub>TiO<sub>3</sub> (Fig 2) shows very broad white lines with crystal-field splitting nearly masked by the width of the L<sub>3</sub> and L<sub>2</sub> features. As in reference spectra of rutile (where Ti is in octahedral coordination) the crystal-field splitting is clearly resolved in similar experimental resolutions conditions, the width of the TiL<sub>23</sub> edge probably arises from the disorder at the Nd sites due to the finite concentration of vacancies which will give a distribution of crystal fields at

the Ti sites. The implications of these changes in the near-edge structure with respect to the electrical properties measurements and the metal-insulator transitions will be discussed and further analysis of the charge-transfer insulator state in the n-type  $\text{Nd}_{1-x}\text{TiO}_3$  material will be presented. These results are compared with spectra obtained in  $\text{BaTiO}_3$  and spatially resolved spectra from grain boundaries in polycrystalline doped and undoped  $\text{BaTiO}_3$  samples.

(1) G. Amow, N.P. Raju and J. E. Greedan, J. Solid State Chemistry, 155, 177-188 (2000).

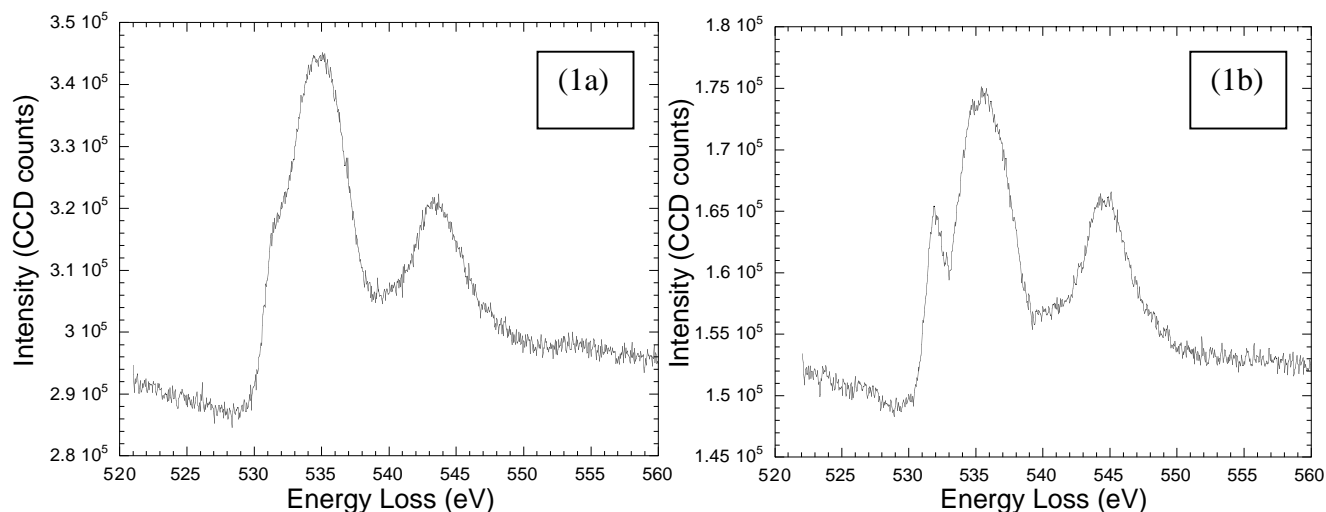


Figure 1. Energy loss fine structures at the O K edges in  $\text{Nd}_{0.95}\text{TiO}_3$  (a) and  $\text{Nd}_{0.88}\text{TiO}_3$  (b). The pre-peak at about 532 eV, arises from the O  $2p$ -Ti- $3d$  hybridization.

Figure 2. Energy loss fine structures at the Ti  $L_{23}$  edge in  $\text{Nd}_{0.88}\text{TiO}_3$ . A very similar fine structure is observed for the  $\text{Nd}_{0.88}\text{TiO}_3$  sample. In rutile, the crystal field splitting is clearly resolved.

