Application of Electron Energy Loss Spectroscopy in the Study of Functional Nanoscale Materials

G. A. Botton¹, C. Maunders¹, L. Gunawan¹, Y. Shao¹, K. Cui¹, L.Y. Chang¹, S. Lazar¹ ²

¹Dept of Materials Science and Engineering, McMaster University, Hamilton, Ont. L8S 4M1, Canada
²FEI Company, FEI Company, Acthseweg Noord 5, 5600 KA Eindhoven, The Netherlands

Electron energy loss spectroscopy provides key information on the electronic properties and bonding of elements in materials. Combined with the high spatial resolution capabilities of an electron microscope, this technique makes it possible to study local variations in composition, coordination and valence in materials used in functional applications. Here we show examples of studies with high-resolution electron energy loss spectroscopy in a range of multiferroic, fuel-cells and quantum materials.

Experiments are carried out on different instruments at the Canadian Centre for Electron Microscopy, including a cryo-UHV STEM (VG HB601), a JEOL 2010F, and a FEI Titan 80-300 Cubed. More recently a FEI Titan 80-300 equipped with a monochromator and aberration corrector of the objective lens and a FEI Titan 80-300 Cubed equipped with a monochromator and two aberration correctors have been installed in our laboratory.

Examples of high resolution imaging in the multiferroic materials BiLaTiO₄ is shown in figure 1. Defects in the Bi-O layers can be readily visible in high-angle annular dark-field imaging. With aberration-corrected imaging, the simplified transfer function and reduced delocalization make it possible to directly visualize growth defects and infer growth mechanisms[1]. Similarly, spectroscopic measurements provide insight on the valence. For example, in the fuel-cell material Cu₁.₂Mn₁.₈O₄, we used the Mn L₂3 edges to identify the fraction of Mn²⁺, Mn³⁺ and Mn⁴⁺ based on the detailed analysis of the Mn L₃/L₂ ratio as well as the fit of the MnL₂₃ near-edge structures. Based on the Cu L edges and the O-K edges, we provided insight into the defect structure and distribution of ions on the tetrahedral and octahedral sites of the spinel structure (figure 2)[2].

When combining high spatial resolution and high energy resolution with simulations, it is possible determine changes in occupancies as well as local changes in electronic structure due to substitutions of transition metals in perovskite compounds. For example, changes in Ti valence in BaTiO₃ are observed when substitutions of Ti ions with Nb are made[3]. Similarly, changes in Ti-Ti bonding are observed when Ru or Mn atoms are replacing Ti atoms in the perovskite structure. These changes are due to the increased metal-metal bonding in the structure arising from the increased proximity of the Ti atoms in face-shared octahedral (figure 3).

In summary, through several examples demonstrating the applications of electron energy loss spectroscopy and high spatial resolution analysis, this presentation will show how electron microscopy techniques can provide additional insight into properties of functional materials.

References

Figure 1. HAADF image of Ba$_{4-x}$La$_x$Ti$_3$O$_{12}$ (x=0.75) with the double layers Bi-O and the perovskite slabs. Highlighted are several stacking defects in the Bi-O layers.

Figure 2. Mn L$_{23}$ edge in Cu$_{1.2}$Mn$_{1.8}$O$_4$ and reference compounds MnO, Mn$_2$O$_3$, MnO$_2$.

Figure 3. Ti L$_{23}$ edges (left) and O K edges (right) in several perovskite compounds.