

Electron Energy Loss Near-Edge Structures in Complex Perovskites

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High-resolution electron energy loss spectroscopy (EELS) provides better sensitivity to fine structures related to bonding in complex materials [1,2]. Using monochromators and improved spectrometers it is possible to achieve 0.1eV resolution with symmetric zero-loss peak profiles leading to improved detection of both core-loss and low-loss features [3] in EELS spectra. This capability makes it possible to study systematically changes in bonding in materials that present interesting physical properties. Oxides with the perovskite structure provide an interesting playing field to study many fundamental changes in structure and physical properties when systematic substitutions of atoms in the crystals are made in a controlled fashion. Substitutions of Ti atoms in BaTiO₃ with other transition metals provide ingenious ways to change the stability of the basic structure and induce phase transformations. For example, Mn substitutions for Ti in BaTiO₃ stabilize the hexagonal phase at room temperature and it has been proposed that this is due to increased metal-metal bonding between adjacent face-sharing octahedra [4]. EELS measurements in Ba(Ti,Mn)O₃, however, have shown that, with respect to the tetragonal structure, there are only subtle changes in the oxygen K edge fine structures of the hexagonal compound due to overlaps of the Mn 3*d* electrons and O 2*p* electrons while the Ti environment is not altered significantly [5]. Ru substitutions for Ti also lead to the stabilization of the hexagonal phase but there are no reports on the effect of the changes in the near-edge structures related to the structural changes. For this particular case, it is of great interest, to study the closely related hexagonal perovskite BaRuO₃. Probing electronic structure changes in these two materials with respect to BaTiO₃ makes it possible to gain insight on both the electronic structure of these closely related compounds and the origin of the structural changes. We have therefore used EELS with high energy resolution to probe the near edge structures in BaTiO₃, Ba(Ti,Ru)O₃ and BaRuO₃.

Experiments were carried out on a FEI Tecnai-200FEG equipped with a monochromator and a high-resolution electron energy loss spectrometer as described previously [1]. While the overall structure of the O-K edge is similar for BaTiO₃ and the compounds with Ru substitutions, there are obvious differences in the details. The first peak at the edge threshold corresponds to the Ti 3*d*-t_{2g} – O 2*p* hybrid bands (or 4*d* bands in BaRuO₃) on the three systems. The peak is increasingly narrower in Ba(Ti,Ru)O₃ and BaRuO₃ as compared to BaTiO₃. At about 2.5eV above the threshold, however, the very weak peak corresponding to the Ti 3*d*-e_g – O 2*p* in BaTiO₃ and Ba(Ti,Ru)O₃ significantly differs from the BaRuO₃. This suggests that in Ba(TiRu)O₃, the Ru 4*d* states strongly overlap with Ti 3*d* electrons and the role of Ru appears to be minor from the electronic point of view. This is in marked contrast with the near-edge structure in the hexagonal BaRuO₃ where there are strong Ru 4*d*-e_g hybrids with the O 2*p* electrons. These latter states have been shown to arise from strong metal-metal bonding between adjacent Ru atoms in face-shared octahedra in recent electronic structure calculations [6]. The calculations also show that these states also strongly hybridize with the O 2*p* bands as suggested in the experimental spectra. The first narrower peak in BaRuO₃ also suggests that differences are present near the Fermi energy of the compounds. In fact, the electronic structure

calculations show that the Fermi energy is located in the middle of the Ru $4d$ t_{2g} band (whether the 4H or 9H hexagonal phase) thus indicating this compound is a metal (or semi-metal) as compared to BaTiO_3 . The trends and discussions based on existing electronic structure calculations show that electron energy loss spectra are therefore good probes of the electronic structure of perovskites and provide invaluable information to test detailed electronic structure calculations. Alternatively, the near-edge structures provide direct insight on the electronic properties of oxides. Similar effects are observed in the $\text{Ba}(\text{Ti},\text{Nb})\text{O}_3$ compound (figure 3) that has been shown to be a metallic oxide[7].

References

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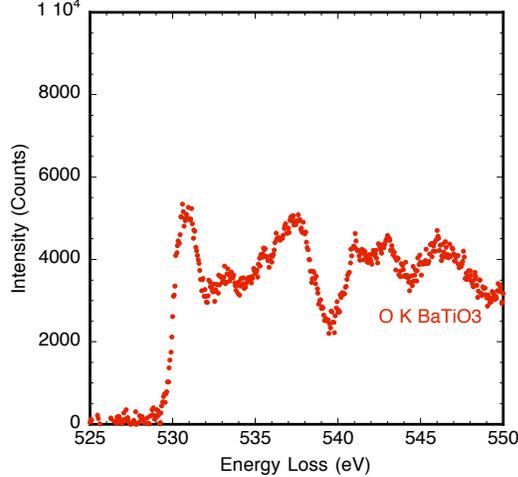


Figure 1) O-K edge in BaTiO_3

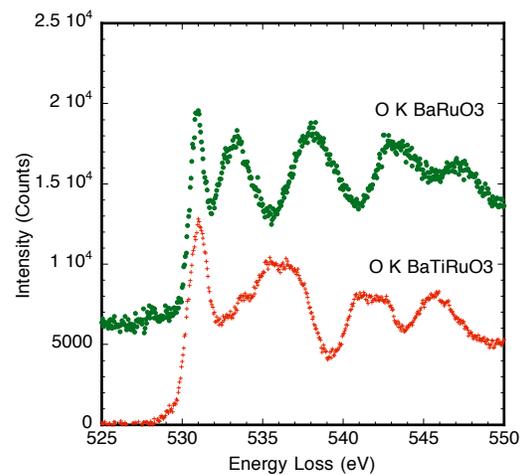


Figure 2) O-K edge in BaRuO_3 and $\text{Ba}(\text{Ti},\text{Ru})\text{O}_3$

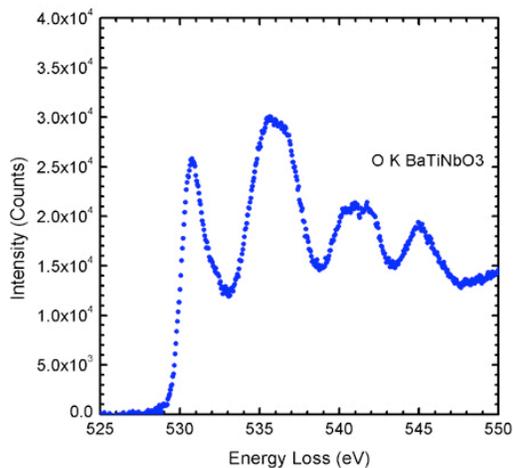


Figure 3) O-K edge in $\text{Ba}(\text{Ti},\text{Nb})\text{O}_3$