Atomic-Scale Studies of Complex Oxide Interfaces Using Aberration-Corrected Z-Contrast Imaging and EELS

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Abstract – The recent development of probe aberration-correctors has enabled us to directly study the atomic-scale structure-property relationships of interfaces in complex oxides. In particular, by using correlated Z-contrast imaging and electron energy-loss spectroscopy (EELS), the structure, composition and bonding at complex oxide interfaces can all be characterized directly with a spatial and energy resolution that cannot be achieved by any other technique. In this paper, we will demonstrate that the combination of Z-contrast imaging and EELS can be used to analyze a wide range of properties in complex oxide materials, such as CMRs, high-κ dielectrics and high-T_c superconductors.

1. Introduction

Interfaces in complex oxide materials have been an enduring theme in materials physics, where the interplay of the reduced dimensionality, proximity effects, as well as surface relaxation, reconstruction and segregation creates interfacial states that are distinct from their bulk counterparts. It has long been recognized that interfaces and grain boundaries in strongly correlated oxide systems can have profound effects the material's properties, creating potentially novel states and behaviors. The combination of aberration-corrected Z-contrast imaging and EELS provides the ability to measure these features directly on a truly atomic scale.

2. Instrumentation

In this presentation, atomic-resolution Z-contrast imaging and column-by-column EELS of interfaces in strongly correlated oxides will be shown. More specifically, we utilize the aberration-corrected JEOL JEM2200FS at Brookhaven National Laboratory (BNL), the aberration-corrected VG HB-601UX at UIC, and the VG HB-501UX at Oak Ridge National Laboratory (ORNL).

The BNL JEOL-JEM2200FS is equipped with a 200 kV Schottky field-emission electron gun, a CEOS probe aberration-corrector [1] and an in-column energy filter. Imaging the dumbbells in a Si [110] sample, we can show that a probe-size of less than 1.0 Å can be achieved (see Figure 1). The VG DSTEMs at ORNL and UIC are equipped with a NION aberration-corrector,[2] a cold-field emission gun and a Gatan Enfina post-column spectrometer, which allows single atom spectrum-imaging.[3]

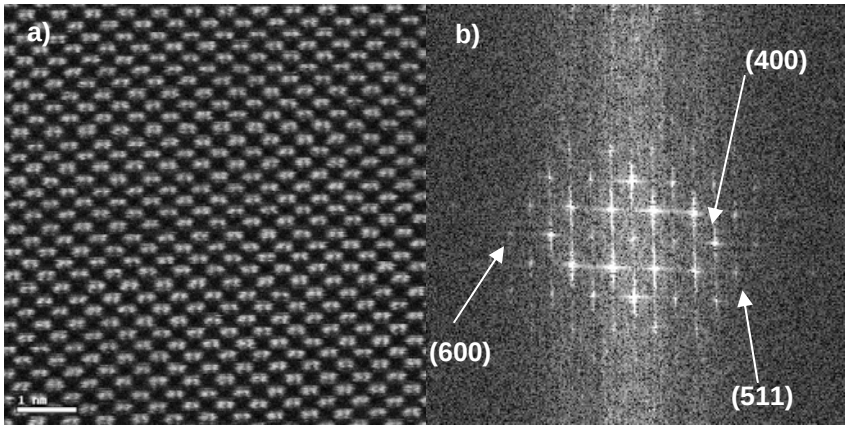

Figure 1: a) Z-contrast image of Si [110] acquired with a probe-convergence angle of 25 mrad, a collection angle of 60 mrad, and an acquisition time of 8.4s. The image clearly shows the two Si-atoms of the dumbbell structure resolved. b) The power-spectrum of a) shows both the (400), (511), as well as the (600) spots, indicating that a probe-size of ~0.907Å can be achieved in the aberration-corrected JEOL-JEM2200FS.

3. Applications

Figure 2 shows a high-resolution Z-contrast image of a pristine and a Ca-doped dislocation core in a 4° [001] tilt grain boundary of $YBa_2Cu_3O_7$ (YBCO). The atomic structure of these two dislocation cores appear to be quite different.[4] Not only do the Ca-doped cores exhibit one additional atomic column on the Y/Ba sublattice (Fig 2b), the Cu-O column right next to the dislocation core appear significantly brighter than any Cu-O column in the bulk, while the third Cu-O column to the right appears significantly darker. Moreover, our EELS spectra show that the local charge carrier concentration in the vicinity of the Ca-doped dislocation core is higher than in the pristine sample.[5] Atomic-column resolved EELS will be used to explore difference in the Cu-O image contrast and measure the profile of the local charge carrier concentration.

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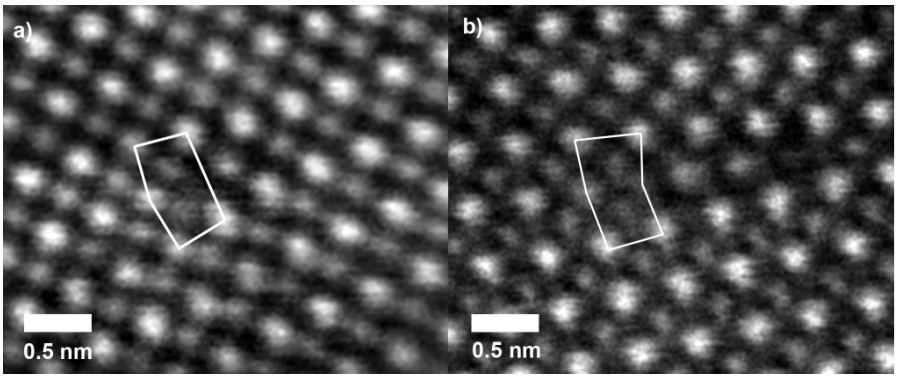

Figure 2: Structural differences in pristine and Ca-doped YBCO. a) Z-contrast image of pristine 4° [001] tilt grain-boundary dislocation core on the Cu-O sublattice. The pentagon shows the center of the dislocation core typically found in perovskite oxide grain boundaries.[4] b) Ca-doped grain-boundary: the Y/Ba column arrangement in the dislocation core encircles three columns, two on the Cu-O and one on the Y/Ba sublattice.

Figure 3 shows an aberration-corrected Z-contrast image of the misfit-layered structure $Ca_3Co_4O_9$, which consists of triple rock salt-type layers Ca_2CoO_3 and single CdI_2-type CoO_2-layers stacked along the *c*-axis (see Fig. 3b).[6] It was previously suggested that the Co-valence alternates from Co^{4+} in the CoO_2-layers to Co^{2+} in the rocksalt layer. The EELS spectra taken from the middle of the rock-salt layer CoO and from the CoO_2 layer (Fig 3c) shows a lower Co-concentration and Co-valence state in the rock-salt layer compared to the spectra taken from the CoO_2 layers. Moreover, the O K-edge pre-peak in the rock-salt layer is significantly lower than in the CoO_2 layers. We will discuss the reduced image contrast in the rocksalt Co-O layers and its influence on the charge transfer at the different Co-sites.

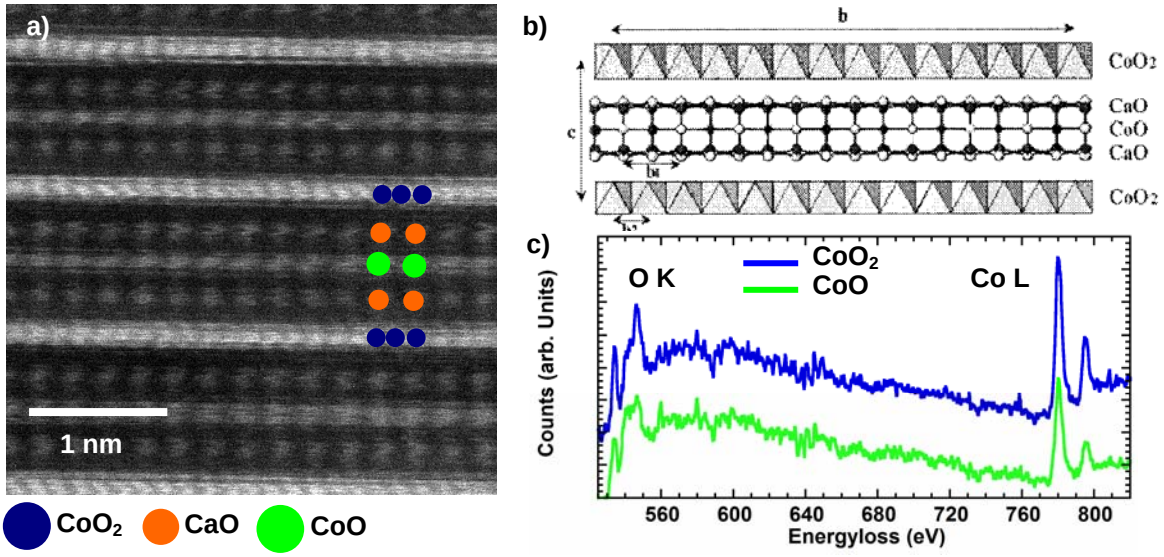

Figure 3: a) Aberration-corrected Z-contrast image of $Ca_3Co_4O_9$ [100]; b) proposed model for this misfit layered structure (taken from [5]); c) EELS spectra taken from the two distinct Co-sites.

4. Conclusions

We have shown that the combination of atomic-resolution Z-contrast imaging and EELS in an aberration-corrected STEM can be used to characterize the effects of charged interfaces and defects in functional nano-materials. In the future, these experiments will be expanded to include in-situ heating and cooling capabilities while maintaining atomic resolution and sub-eV energy resolution.

5. References

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