doi: 10.1017/S1431927609094422
Microsc Microanal 15(Suppl 2), 2009

Atomic-resolution STEM and variable-temperature EELS Studies of Thermoelectric $Ca_3Co_4O_9$

G. Yang*, Q. Ramasse**, R. F. Klie*

* Department of Physics, University of Illinois at Chicago, 845 W. Taylor St., Chicago, IL, 60616
** National Center for Electron Microscopy, Lawrence Berkeley National Laboratory, Berkeley, CA 94720

The misfit-layered cobalt oxide $Ca_3Co_4O_9$ exhibits outstanding physical properties including high thermoelectric power, low thermal conductivity, low resistivity and high thermal stability [1]. We utilize atomic-resolution Z-contrast imaging in conjunction with electron energy-loss spectroscopy (EELS) in aberration-corrected scanning transmission electron microscope (STEM) to characterize the local atomic and electronic structures of $Ca_3Co_4O_9$.

In our study, the atomic-resolution STEM images were obtained using the TEAM0.5 instrument (FEI Titan 300 kV TEM/STEM) and in order to minimize the electron irradiation damage, all EELS spectra were obtained using an aberration corrected VG HB 501 dedicated STEM. Figure 1a) shows an atomic-resolution Z-contrast image of $Ca_3Co_4O_9$ (taken from TEAM0.5) in the [010] orientation, clearly exhibiting the four distinct layers of varying brightness. The CoO_2 layer can be seen as the brightest layer followed by the CaO, CoO and CaO layer, respectively. The incommensurate structure of $Ca_3Co_4O_9$ is not visible in this orientation. The atomic arrangements are consistent with the simulated Z-contrast image at the same orientation (Figure 1b), except the blurred CoO layers. It is found recently, by X-ray diffraction analysis, that the middle CoO layers are much complicated than all other layers, and a triple chain configuration was suggested to explain the complexity of these layers [2]. That might explain the apparent faintness of the CoO layers contrast in Fig. 1a. The other surprising finding is the direct visualization of O atomic columns in CoO_2 layers. Figure 1c) shows an intensity profile taken across a Co and O atomic columns in the CoO_2 layer. Here, the Co columns are shown as the brightest intensity peak, while the shoulders on both sides correspond to the positions of the O atomic columns, whose relative intensities are right for O compared to Co intensity using a Z^2 argument [3].

Atomic-column resolved electron energy-loss spectra (taken from VG HB501) of the different layers in the $Ca_3Co_4O_9$ unit-cell are shown in Figure 2. There are three main peaks in the background subtracted oxygen K-edge spectra, and all spectra are normalized to peak C. The intensity of peak A in CoO_2 layers are higher than that from CoO layers, which could be attributed to the charge transfer between the Co layers[4]. Figure 3 shows the Co L-edge from the CoO_2 and the CoO, respectively. By using the relationship between the Co $L_3\backslash L_2$-ratio and the Co valence, we find that a mixed valence state exists in the in the CoO_2 layers with a nominal Co valence of 3.5+, while the valence in the CoO layers is 3.0+. The difference of measured Co valences compared with nominal oxidation states in both layers indicates a charge transfer between Co layers, which provides mobile holes to the CoO_2 layer and is responsible for the high 2-dimensional electrical conductivity [5].

In our presentation we will further discuss the effects of charge transfer and Co-ion spin states transitions on the high-temperature conductivity in $Ca_3Co_4O_9$ using variable temperature EELS. And also the effects of the electron irradiation damage on the microstructure of $Ca_3Co_4O_9$ will be shown.

References:

[1] A. C. Masset et al., Phys Rev B **62**, 166 (2000)
[2] H. Muguerra,et al., Acta Crystallogr. Sect. B-Struct. Sci, **64**, 144 (2008).
[3]S. J. Pennycook, and L. A. Boatner, Nature **336**, 565 (1988)
[4] N. D. Browning et al, Physica C **212**, 185 (1993).
[5] G. Yang et al, Phys. Rev. B **78**, 153109 (2008).

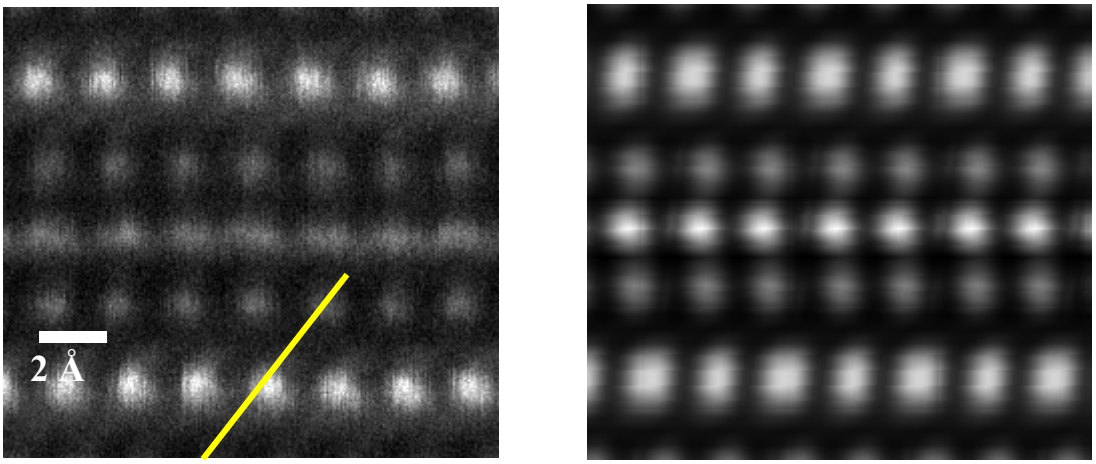
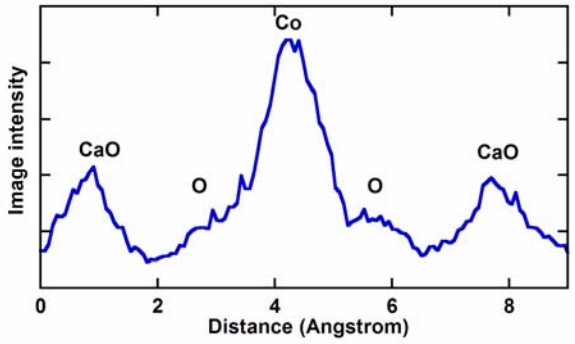


Figure 1: a) Z-contrast image of $Ca_3Co_4O_9$ [010]; **b)** Simulated Z-contrast image of $Ca_3Co_4O_9$ [010]



c) Intensity profile of the image across a Co atomic column and two adjacent O columns (as shown in Figure 1a)

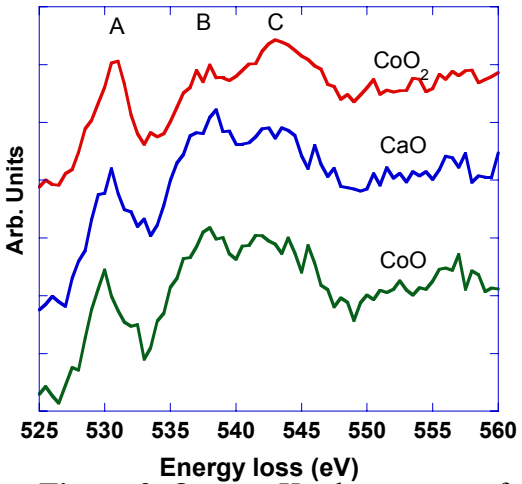


Figure 2. Oxygen K-edge spectra of different layers in $Ca_3Co_4O_9$

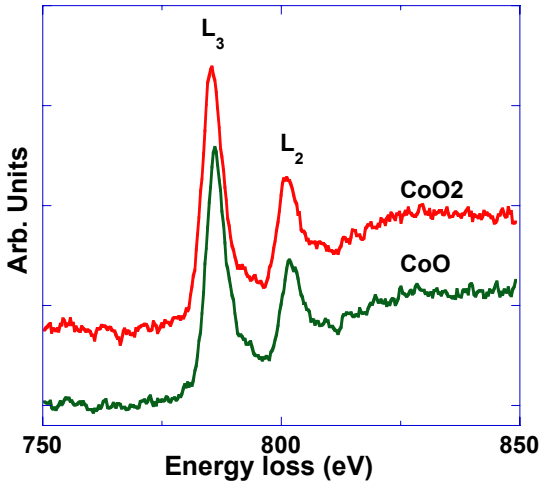


Figure 3. Co L-edges for the different Co-O layers showing the Co L_3 and the L_2

https://doi.org/10.1017/S1431927609094422 Published online by Cambridge University Press