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

G.Yang[1,3], Q. Ramasse[2], R. F. Klie[1], E. Spiecker[3]

1. Department of Physics, University of Illinois at Chicago, 845 W. Taylor St., Chicago, IL, 60616, USA
2. National Center for Electron Microscopy, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA
3. Department for Materials Science, University of Erlangen-Nürnberg, Erlangen, Germany

guang.yang@ww.uni-erlangen.de
Keywords: STEM, EELS, aberration corrected, thermoelectric

As a potential candidate material for practical thermoelectric devices, the misfit-layered cobalt oxide $Ca_3Co_4O_9$ has drawn extensive attention from both physicists and chemists due to its outstanding physical properties including high thermoelectric power, low thermal conductivity, low resistivity and high thermal stability [1]. We utilize atomic-resolution Z-contrast imaging combined with electron energy-loss spectroscopy (EELS) in an aberration-corrected scanning transmission electron microscope (STEM) to characterize the local atomic and electronic structures of $Ca_3Co_4O_9$.

In this study, the atomic-resolution Z-contrast images were obtained using the TEAM0.5 instrument (FEI Titan 300 kV TEM/STEM), and all EELS spectra were obtained using an aberration corrected VG HB 501 dedicated STEM in order to minimize the electron irradiation damage. Figure 1a) shows the 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 incommensurate structure of $Ca_3Co_4O_9$ is not visible in this orientation. The CoO_2 layer can be seen as the brightest layer followed by the CaO, CoO and CaO layers, respectively. The atomic arrangements are consistent with the simulated Z-contrast image at the same orientation (Figure 1b), except the blurred CoO layers. The recently proposed triple chain configuration in the CoO layers explains the apparent faintness of the CoO layers contrast. The other surprising finding is the direct visualization of O atomic columns in CoO_2 layers. Figure 1c) shows an intensity profile across 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 EELS spectra (obtained 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 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 2D electrical conductivity [5].

In our presentation we will also discuss the effects of charge transfer and Co-ion spin state transitions in $Ca_3Co_4O_9$ using in situ heating experiments. Furthermore the effects of the electron irradiation damage on the microstructure of $Ca_3Co_4O_9$ will be shown.

W. Grogger, F. Hofer, P. Pölt (Eds.): MC2009, Vol. 3: Materials Science,
DOI: 10.3217/978-3-85125-062-6-399 , © Verlag der TU Graz 2009

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

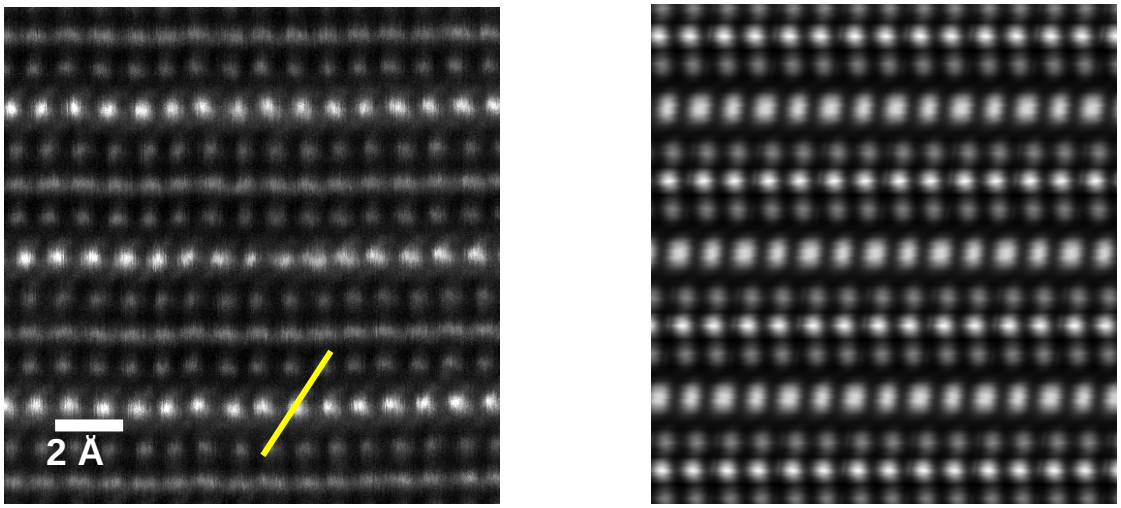
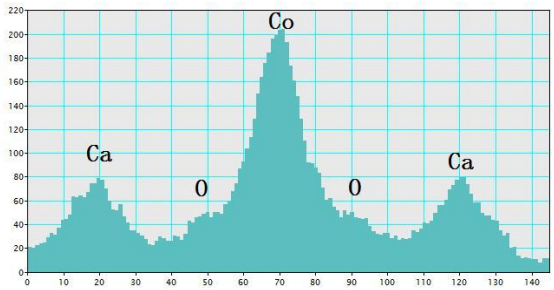


Figure 1 a) Z-contrast image of $Ca_3Co_4O_9$ [010]; **b)** Simulated Z-contrast image of $Ca_3Co_4O_9$ [010]



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

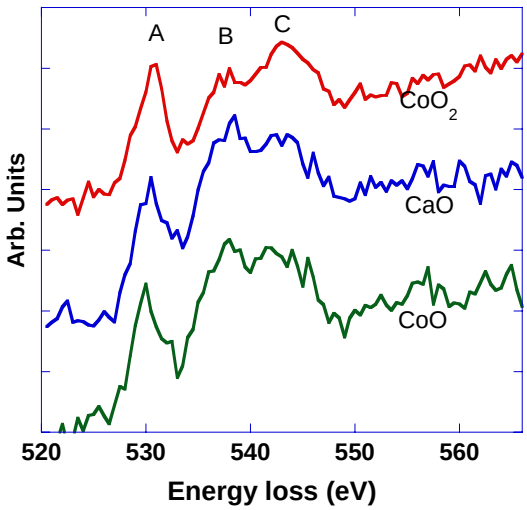


Figure 2. Oxygen K-edge spectra of different layers in $Ca_3Co_4O_9$

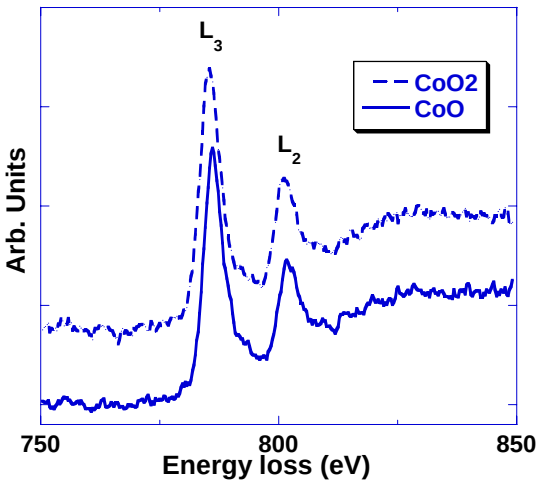


Figure 3. Co L-edges for the different Co-O layers showing the Co L_3 and the L_2

DOI: 10.3217/978-3-85125-062-6-399 ,