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Atomic-Resolution Annular Bright-Field and Spectrum Imaging of Incommensurately-layered $Ca_3Co_4O_9$

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The misfit-layered oxide $Ca_3Co_4O_9$ exhibits outstanding physical properties including high thermoelectric power, low thermal conductivity, low resistivity and high thermal stability [1]. It has been shown that changes in the local valence state of Co and interfacial strain can result in significant changes in the material's Seebeck coefficient, S [2]. Therefore, in this study we utilize atomic-resolution Z-contrast imaging, annular bright-field imaging as well as electron energy-loss spectrum imaging in an aberration-corrected JEOL ARM-200F to characterize the local atomic and electronic structures of bulk $Ca_3Co_4O_9$.

$Ca_3Co_4O_9$, an incommensurately layered oxide, can be best described as a monoclinic structure with two misfit-layered subsystems, a distorted rocksalt-type Ca_2CoO_3 layer sandwiched between two CdI_2-typed CoO_2 layers along the c-axis, which makes it an ideal system for studying effects such as charge transfer, strain and spin-state transitions on the material's thermoelectric behavior. Both subsystems share the same lattice parameters with $a=4.8339$ Å, $c=10.8436$ Å and $\beta=98.14°$, but along b-axis the incommensurate structure results in $b_1= 2.8238$ Å for the CoO_2 subsystem and $b_2=4.5582$ Å for the Ca_2CoO_3 subsystem. Previously, using atomic-column-resolved EELS and in-situ heating experiments, we have demonstrated that there is significant charge transfer between the Co-ions in the insulating rocksalt layers and the metallic CoO_2-layers. In addition, we could show that at high temperature the Co-ion spin-states undergo a transition into a higher spin-state without any structural transition [3-4].

Figures 1 and 2 show atomic-resolution Z-contrast and annular bright field (ABF) images obtained with a convergence angle of 22 mrad at 200 kV using an annular detector with an inner angle of 11 mrad and an outer angle of 22 mrad for ABF imaging. The ABF images show the positions of all the atomic columns present in the $Ca_3Co_4O_9$ unit-cell, and no contrast reversal due to changing defocus or sample thickness was observed. In Figure 2b) the positions o the oxygen atomic columns in the rocksalt layers can be clearly seen, while the O in the CoO_2 layers show up as blurred lines, since the CoO_2 is not oriented along a zone-axis. Figure 3 shows an atomic-column resolved EELS spectrum image acquired from $Ca_3Co_4O_9$ [110]. Displaying only the integrated intensities of the Co L-edge, the Ca L-edges and the O K-edge (Figure 3a) we can determine the position and local composition of the $Ca_3Co_4O_9$ unit-cell. Using the O K-edge pre-peak intensity and the Co L_3/L_2-ratio, we can map the local bonding within the $Ca_3Co_4O_9$ unit-cell.

In our presentation we will discuss how the combination of atomic-resolution Z-contrast imaging, ABF and EELS spectrum imaging can be used to determine the effects of structural disorder, strain and charge transfer on the thermoelectric properties of $Ca_3Co_4O_9$-based materials [5].

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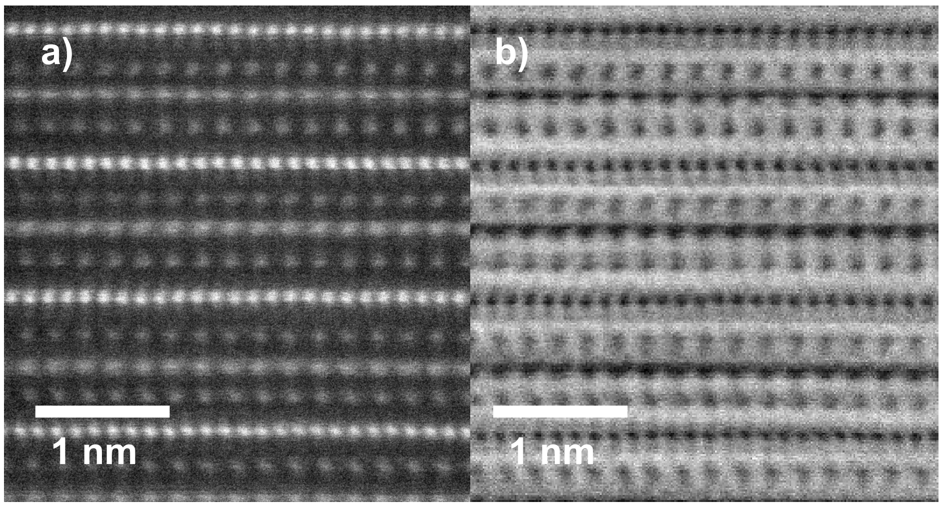

Figure 1: Atomic-resolution a) Z-contrast image and b) annular bright field image of $Ca_3Co_4O_9$ [100] showing the triple rocksalt layers sandwiched between CoO_2.

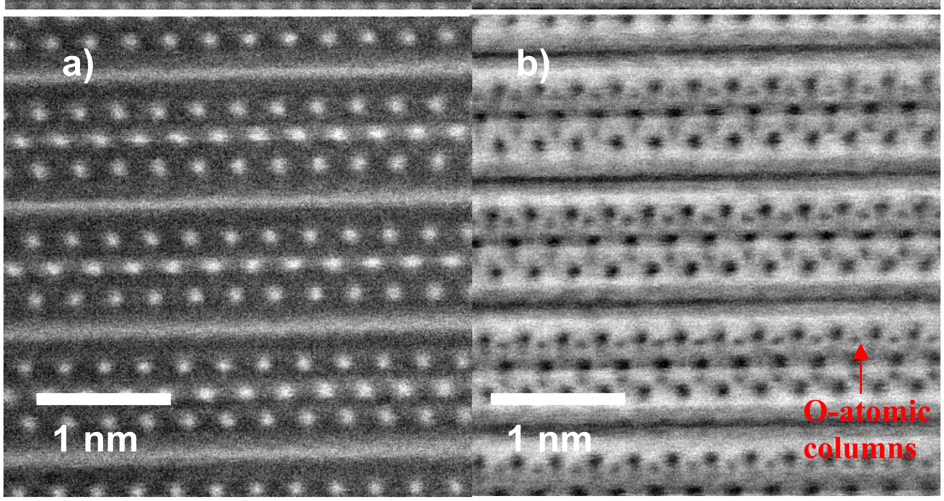

Figure 2: Atomic-resolution a) Z-contrast image and b) annular bright field image of $Ca_3Co_4O_9$ [110]. In this projection the O atomic columns are clearly visible in the annular bright field image.

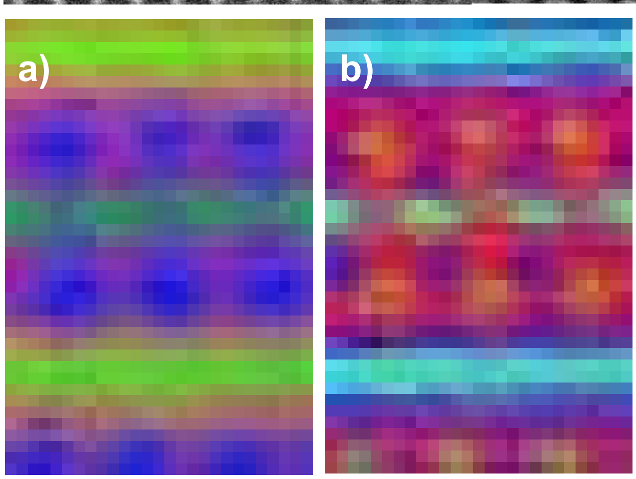

Figure 3: Atomic-resolution EELS spectrum image of $Ca_3Co_4O_9$ [110] showing: a) the integrated intensities of Co (green), Ca (blue) and O (red); b) the Co L_3/L_2 ratio (blue), the O K-edge pre-peak intensity (red) and ADF signal (blue).

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