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How Dopants and Defects Affect the properties of Thermoelectric $Ca_3Co_4O_9$

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Thermoelectric oxides have attracted increasing attention due to their high thermal power and temperature stability.[1] In particular, $Ca_3Co_4O_9$ (CCO), a misfit layered structure consisting of single layer hole-doped CoO_2 sandwiched between insulating Ca_2CoO_3 rocksalt layers, exhibits a high Seebeck coefficient at 1000 K. It was suggested that the Seebeck-coefficient can be further increased by growing doped thin films with controlled defects structures.[2] This study combines pulsed layer deposition thin film synthesis of pristine CCO on several oxide substrates, as well as CCO thin films doped with Ti, Bi or La, with aberration-corrected scanning transmission electron microscopy and electron energy loss spectroscopy (EELS) in the JEOL ARM200-CF to examine the effects of interfacial strain and doping on the atomic and electronic structures of CCO. The thermoelectric properties will be measured and correlated to the local changes in the atomic and electronic structures. We will further evaluate the role of CoO_2 stacking faults, as well as film thickness on the thermoelectric properties of CCO.

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 shows atomic-resolution Z-contrast images of bulk CCO and a 40 nm thin CCO film on $SrTiO_3$. The thin film exhibits a significant increase in the Seebeck coefficient, and a high density of stacking faults, as well as *ab*-plane rotation. Moreover, the thin films appear unstrained, although the lattice mismatch between the $SrTiO_3$ (001) substrate ad the CCO (001) thin film is 14.3%. Figure 2 shows an atomic-column resolved EELS spectrum image of the area marked in Figure 1b). The integrated Co L-edge intensity shows that the stacking faults consist of a double CoO_2 layer, while the relative O K-edge pre-peak exhibits its highest intensity on the O-atomic columns of teh CoO_2 layers. The relative O K-edge pre-peak intensity is significantly increased in the stacking fault (Figure 2c), pointing to a higher mobile hole concentration or Co-ion spin state. The effects of Ti doping in CCO are explored in Figure 3, which shows a Z-contrast image of a $Ca_3Co_{3.8}Ti_{0.2}O_9$ thin film. It can be clearly seen that Ti does not replace Co but instead sits in the Ca atomic columns, and does therefore not induce any strain or provide additional mobile holes to the CoO^2 layers.

In our presentation we will discuss how the combination of atomic-resolution Z-contrast imaging, EELS spectrum imaging and transport measurements can 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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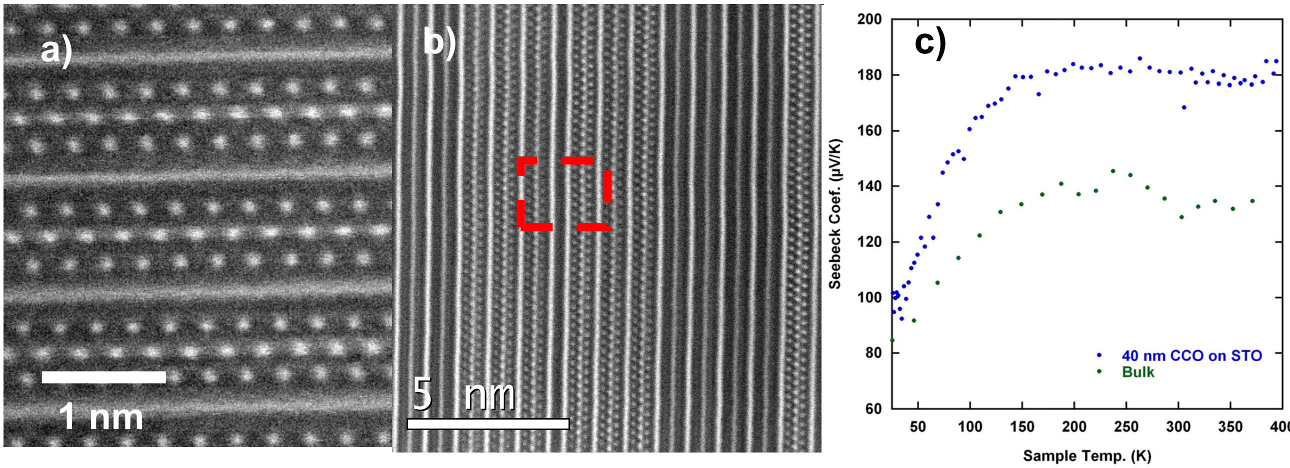

Figure 1: Atomic-resolution Z-contrast image of $Ca_3Co_4O_9$ [110] of a) bulk and b) the 40 nm thin film on $SrTiO_3$ showing CoO_2 stacking fault. c) Seebeck coefficient for both samples.

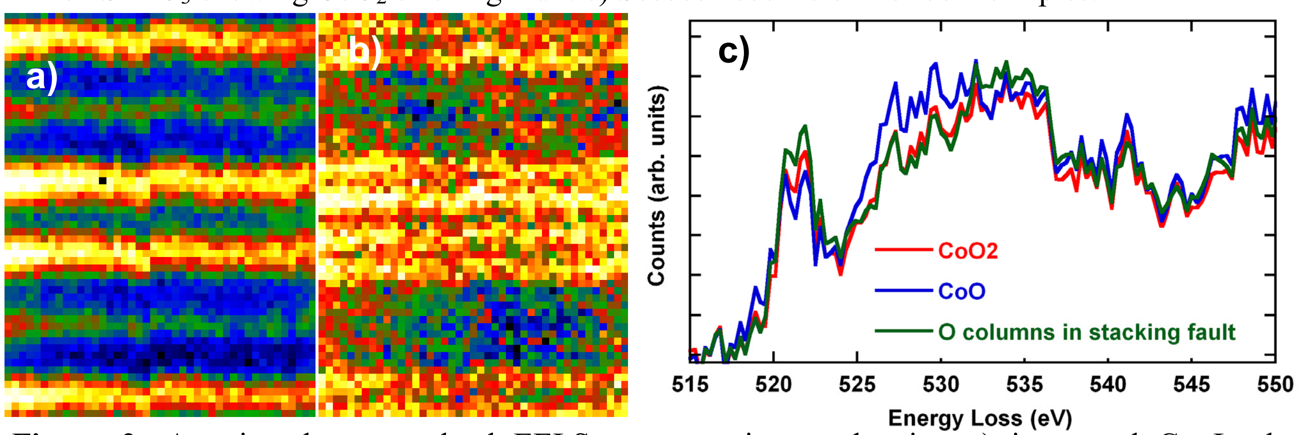

Figure 2: Atomic-column resolved EELS spectrum image showing a) integrated Co L-edge intensity, b) relative O K-edge pre-peak intensity across CoO_2 stacking fault. c) O K-edge fine structure for the different layers in CCO, showing the increased pre-peak in the CoO_2 stacking fault.

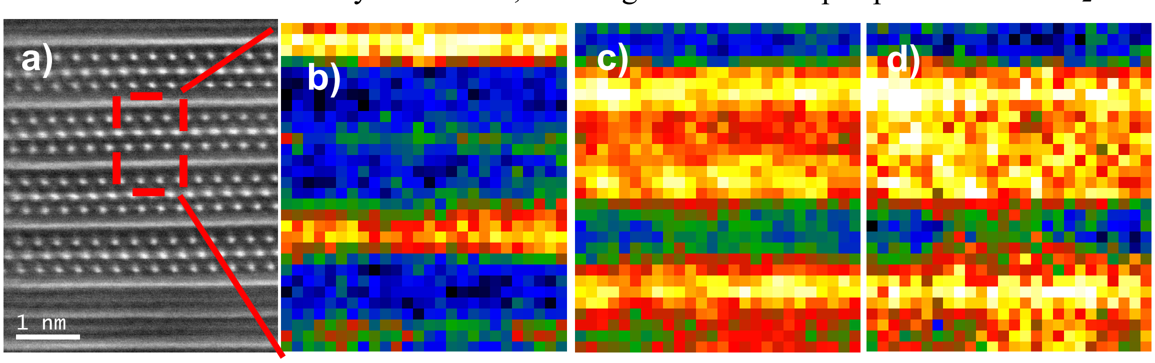

Figure 3: a) Atomic-resolution Z-contrast image of $Ca_3Co_{3.8}Ti_{0.2}O_9$ thin film. b-d) Atomic column resolved spectrum image of the b) Co c) Ca and d) Ti L-edges showing that the Ti dopants are replacing Ca atoms rather than Co.

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