# Atomic-Resolution EELS Study of Titanium Dopant Effects of $Ca_3Co_4O_9$ Thin Film

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Thermoelectric materials have attracted significant attention over the last few decades. As one of the outstanding thermoelectric oxide materials, the incommensurately layered $Ca_3Co_4O_9$ (CCO) exhibits a high in-plane Seebeck coefficient and a high thermoelectric figure of merit at high temperature. Many studies have reported that substitutional doping will increase the Seebeck coefficient [1], but understanding of dopant effects on local structure and electronic properties is still lacking. Using electron energy-loss spectroscopy (EELS) and first-principle calculations, the atomic and electronic structure of Ti dopants can be measured and the dopant effects on the thermoelectric properties can be analysed.

Ti-doped CCO thin films ($Ca_3Co_{3.8}Ti_{0.2}O_9$) were deposited by Pulsed Laser Deposition (PLD). All the images and EEL spectra were acquired by using an aberration-corrected JEOL ARM200CF with a 200 kV cold field emission gun and post-column Gatan Enfina EELS spectrometer. Figure 1a-c) shows the EELS image of Co, Ti, and Ca signals, respectively. The integrated signal intensity of Ti $L$-edge has been used to determine the position of Ti dopants. We find that the Ti dopants mainly replace Co atoms in the $Ca_2CoO_3$ subsystem. We have analysed the near edge fine-structure of the Ti $L$-edge and compared it to the shape of reference spectra for $Ti^{4+}$ and $Ti^{3+}$ [2]. We determine the valence state of Ti to be 4+. Figure 1c) shows the Co $L_3/L_2$ ratio as a function of concentration ratio of Ti/Ca. As the Ti concentration increases, the intensity ratio of Co $L_3/L_2$ remains mostly unchanged. Since the Co white lines ratio is directly linked to the Co valence state [3], we determine the Co valence state of $CoO_2$ subsystem to be ($3.4 \pm 0.2$) and the Co valence in the $Ca_2CoO_3$ subsystem to be ($2.8 \pm 0.2$). The results are close to the values of the Co valence of pristine CCO bulk [4]. This demonstrates that the Ti doping does not influence the Co valence, especially the mixed-valence state of Co in $CoO_2$ layer, which means that hole concentration in the $p$-type $CoO_2$ layers remains unchanged and the effect of Ti doping on the Seebeck coefficient should be negligible.[5]

The experimental results will next be tested using first principles DFT modelling. Figure 2a) shows the unit cell of pristine 5/3 CCO with 66 atoms, which is used in our first-principle calculations. Based on this structure, the Ti dopants are studied by substituting Ti atom for one of the Ca atoms and Co atoms. All the 12 Ca sites and 16 Co sites have been considered. The calculated total energies show that Ti dopants are preferred on the Co sites of $Ca_2CoO_3$ subsystem compared to the Co sites of the $CoO_2$ layer, which is in agreement with our experimental observation. Figure 2b) shows the partial density of states (PDOS) of angular –momentum resolved $d$-orbitals of the Ti atom, substituting the Co atom of the $Ca_2CoO_3$ subsystem, where all the Ti $3d$ orbitals are empty. In addition, the PDOS of the Ti $p$-orbitals shows that the Ti $3p$ orbitals are completely occupied. We can conclude that the valence of Ti dopant is 4+. However, the effects of Ti dopants and their locations on local electronic structure is still being examined.

In this presentation, we will discuss out latest EELS result combined with first-principle calculations to analyse how Ti dopants influence the thermoelectric performance of CCO thin film [6].

References:

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[5] W. Koshibae *et al*, Physical Review B **62** (2000), p. 6869-6872.
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**Figure 1:**
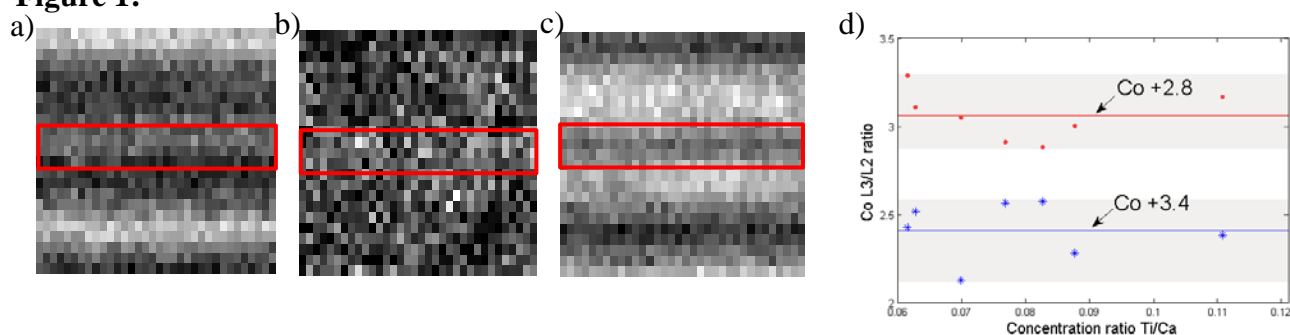


**Figure 1.** Ti doped $Ca_3Co_4O_9$ thin film along [110]: a-c) EELS images for Co, Ti, and Ca signals, respectively. The red rectangle is the area of CoO column of $Ca_2CoO_3$ subsystem. d) Intensity ratio of Co $L_3/L_2$ as a function of concentration ratio of Ti/Ca, for Co in $CoO_2$ layer (blue stars) and Co in CoO column of RS subsystem (red spots).

**Figure 2:**
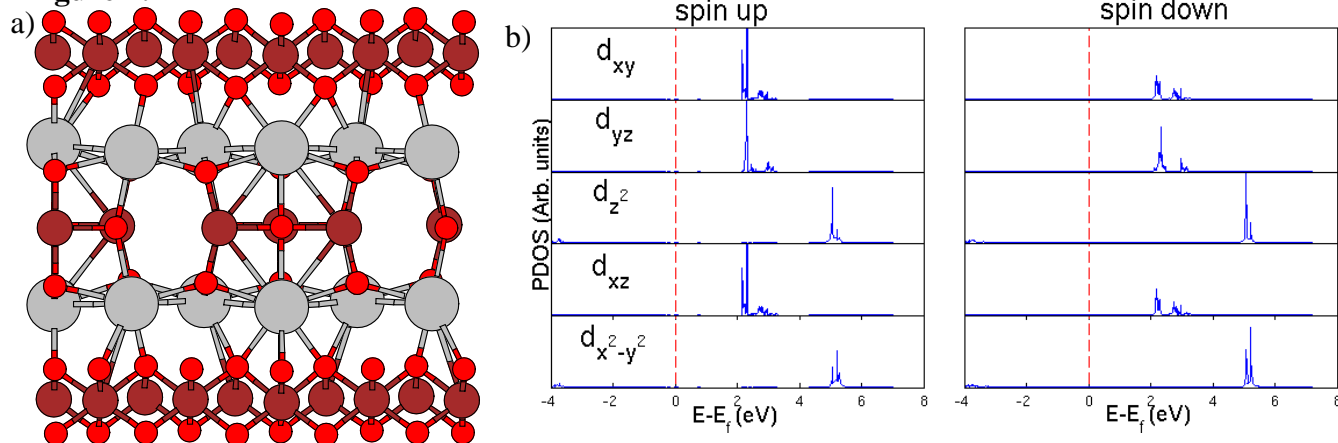


**Figure 2.** First-principle simulation of Ti doped $Ca_3Co_4O_9$: a) the unit cell of pristine 5/3 CCO with 66 atoms; b) the partial density of states (PDOS) of m-resolved d orbitals of Ti atom, which substitutes the Co atom of RS subsystem.