EELS analyses at grain boundaries in CaCu$_3$Ti$_4$O$_{12}$

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CaCu$_3$Ti$_4$O$_{12}$ (CCTO) is one of a family of phases with a perovskite-related structure (general formula ABO$_3$) in which Ca$^{2+}$ and Cu$^{2+}$ ions share the A-site [1]. CCTO exhibits high permittivity at room temperatures [2] and so is of interest as a capacitor. The observed high permittivity is believed to be due to an extrinsic effect associated with electrical heterogeneities, such as insulating grain boundary layers between semi-conducting grains. Although much work has been carried out on the electrical properties of CCTO [3, 4], there is virtually no microscopy based information available to relate the observed electrical properties to the microstructure and chemistry on the nanometre scale.

EELS, EDS and HREM have been undertaken on samples of CCTO that have been sintered for 24 hours at 1100°C in air. The sintered CCTO has a grain size of 100-300 microns. Many of the grain boundaries were free from an amorphous phase although such a phase was occasionally observed. The majority of grain boundaries exhibited a step-like morphology and high local stress, suggesting that they were dominated by grain boundary specific changes in chemistry or structure. Discrete particles were also observed within grain boundaries that could not be uniquely identified, but were shown to be Cu rich. EEL data were collected for bulk CCTO (within grain) and simultaneously with EDS at grain boundaries. The bulk EEL data suggest that Cu is divalent and Ti is present as Ti$^{4+}$. EEL data for the grain boundaries suggest that Cu becomes mixed valence, and Ti has a trivalent component. These valence changes are also reflected by changes in the NES of the associated O K-edge. The EDS data collected at the grain boundaries also suggests changes in the Ca/Ti/Cu ratios.

![Image of EELS and EDS data](image_url)

Figure 1 comparing grain boundary Ti L$_{2,3}$ and Cu L$_{2,3}$-edges (1) with bulk data (2)

References

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