Characterisation of Grain Boundaries in CaCu$_3$Ti$_4$O$_{12}$ using HREM, EDS and EELS.

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Abstract. Preliminary EELS and EDS analyses undertaken on CaCu$_3$Ti$_4$O$_{12}$ ceramics, sintered for 3 and 24 hrs at 1100°C in air, have suggested that there are differences in the composition and valence of the Cu and Ti at grain boundaries as compared with the bulk composition. For the 3 hour sinter a change was observed in the Cu valence and for the 24 hour a change in both Ti and Cu valences was detected. This variation in composition may explain the electrical properties of high permittivity at room temperature exhibited by these ceramics.

1. Introduction

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 ceramics exhibit high permittivity at room temperature [2] and are therefore of interest as capacitor materials. 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] and [4], there is virtually no microscopy based information available to relate the observed electrical properties to the microstructure and chemistry on the nanometre scale. Here we present preliminary EELS, EDS and HRES imaging of grain boundaries, undertaken on samples of CCTO that have been sintered for 3 and 24 hours at 1100°C in air.

2. Experimental

CCTO ceramics were prepared by standard sintering, as described in [5]. All EELS analyses were carried out using a GIF2000, attached to a JEOL JEM 2010F microscope, operated at 200keV with a filament emission of ~60-80µA. The samples were polished to optical transparency using P2500 SiC paper and finished using 3 µm diamond paste on silk, mounted on 3mm Ni support grids and thinned using a Gatan DuoMill 600.

EELS measurements were made in diffraction mode (image coupling to spectrometer) on thin (<30nm) crystalline areas. All spectra were corrected for dark count and detector gain. Grain boundary data were collected using a 1 nm probe formed using the JEOL EDS mode. For each grain boundary, a series of spectra were collected; in the bulk, adjacent to the grain boundary and on the grain boundary. Ti L$_{2,3}$- , Cu L$_{2,3}$- and O K-edges were collected, with total integration times of 25 seconds for O K- and Ti L$_{2,3}$-edges and 50 seconds for Cu L$_{2,3}$-edges at an energy dispersion of 0.1eV/pixel. Low loss spectra were collected close to the grain boundary in TEM diffraction mode rather than EDS (diffraction) mode to avoid overloading the CCD. The energy resolution for all measurements was 1.0-1.1eV. All spectra were energy calibrated by collection of a 0.3eV dispersion spectrum containing the C K-edge.
(calibrated at 285eV), Ca and Ti L$_{2,3}$-edges and the O K-edge. Finally, the spectra presented here have been background subtracted, using a power law function and intensity normalised for ease of comparison.

3. Results and Discussion

![Figure 1](image1.png)

**Figure 1** a) BF image of a GB in the 24 hour sinter CCTO, showing the presence of Cu rich particles b) BF image showing a typical stepped GB in CCTO.

![Figure 2](image2.png)

**Figure 2** Showing the changes in (a) the Ti L$_{2,3}$-edge and (b) the Cu L$_{2,3}$-edge in a traverse across a grain boundary in 24 hour sinter CCTO.
The majority of grain boundaries imaged exhibited a step-like morphology (Fig. 1b) and high local stress, suggesting that they were dominated by grain boundary specific changes in chemistry or structure. They were generally free from an amorphous phase although such a phase was occasionally observed. Discrete particles were also observed within grain boundaries (Fig. 1a & 3a) and at triple points in the three hour sinter that were shown to be Cu rich (Fig. 3b & 4b). The bulk EELS data suggest that Cu is divalent and Ti is present as Ti$^{4+}$. EELS data for the grain boundaries suggest that the transition metals show changes in valence both approaching and at the grain boundaries. Cu becomes mixed valence (Cu$^{2+}$/Cu$^{+}$) indicated by increased intensity at ~934 eV (arrowed on Fig 2 b)), and Ti has a trivalent component, indicated by a decrease in intensity of peaks 1 and 3 as compared with the bulk data, for the 24 hour sinter (Fig. 2a) and b)) and Cu also becomes mixed valence in the 3
hour sinter (Fig. 4a). The EDS data collected at the grain boundaries also suggests changes in the Ca/Ti/Cu ratios.

4. Preliminary Conclusions

Comparing the EELS data for CCTO [6] with known standards reveals that the Ti L_{2,3}-edge shows a similar NES to that of rutile and CaTiO₃ (Ti⁴⁺ in a slightly distorted octahedral co-ordination with O). The Ca L_{2,3} and Cu L_{2,3}-edges both match well with published data for Ca²⁺ and Cu²⁺. The grain boundaries in the 24 hour sinter are stepped rather than smooth, suggesting that they are not dominated by interfacial energy, but by changes in the chemistry or structure of CCTO. EDS and EEL analysis of the grain boundaries in both the 3 and 24 hour sinter CCTO suggests that there is evidence of segregation of Si (contamination from ball milling of the powders) and some Ca. This has been confirmed using EFTEM. Beam damage of CCTO ceramics appears to be a problem during long analysis times (>150 seconds total acquisition) for EELS in focussed probe mode and EFTEM, and could be an important factor in interpretation of the data. EDS data for the 24 hour sintered sample suggest there is a change in the Ca/Ti/Cu ratio at the grain boundaries, with a decrease in Ti relative to Ca and Cu.

For the 24 hour sintered samples, data collected in traverses across grain boundaries suggests that there is a change in the NES of the O K-, Ti L- and Cu L_{2,3}-edges. These changes appear to suggest that there is a change in Cu valence from Cu²⁺ to Cu¹⁺, with the associated change in O-Cu hybridisation seen in the O K-edge. The changes in the Ti L_{2,3}-edge may either be a change in valence from Ti⁴⁺ to mixed Ti³⁺/Ti⁴⁺ or a change in the distortion of the TiO₆ octahedra. For the 3 hour sinter samples there was only a change in the Cu valence, from Cu²⁺ to mixed Cu²⁺/Cu¹⁺. Impedance spectroscopy has suggested that the bulk CCTO should be semi-conducting with insulating grain boundaries. If Cu valence changes from Cu²⁺ to Cu¹⁺ and Ti to mixed Ti³⁺/Ti⁴⁺ this would suggest a conducting grain boundary. Another possible explanation would be the presence of O vacancies at the grain boundary. Further work using facilities with improved EELS energy resolution and spatial resolution is needed to explain this fully.

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