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ATOMIC-RESOLUTION CHARACTERIZATION OF INTERFACE STRUCTURE AND CHEMISTRY IN THE STEM

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Atomic Resolution Characterization of Interface Structure and Chemistry in the STEM

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1. INTRODUCTION

Recent developments in the scanning transmission electron microscope (STEM) have enabled electron energy loss spectroscopy (EELS) to be used to determine elemental compositions (Browning et al (1993)) and map the local electronic structure (Batson (1993)) at interfaces on the atomic scale. This high spatial resolution spectroscopy is obtained by using an atomic resolution high-angle annular dark field or "Z-contrast" image (Pennycook and Jesson (1990)) to position the probe. The Z-contrast image, being incoherent in nature, allows the intuitive interpretation of interface structures without the need for preconceived models and, as only the high-angle scattering is used for the image, EELS can be performed simultaneously from a single atomic column defined by the image. The combination of Z-contrast imaging and EELS thus allows the local structure and chemistry of interfaces to be determined on the atomic scale. In this paper, we use these two complimentary techniques to analyse the structure and chemistry of a nominally 25 degree [100] symmetric tilt boundary in a bicrystal of the electroceramic $SrTiO_3$.

2. INTERFACE CHARACTERIZATION

A Z-contrast image of a symmetric region of the grain boundary is shown in figure 1(a). In the image the brightest spots correspond to the positions of the strontium columns, Z=38, with the less bright spots being the positions of the titanium columns, Z=22, (oxygen columns are not imaged). In figure 1(b) the maximum entropy image processing technique (Gull and Skilling (1984)) is used to enhance the contrast so that the positions of the metal atom columns in the grain boundary can be clearly observed. Using the Z-contrast image to position the probe, oxygen K-edge and titanium L-edge spectra were taken in single unit cell steps across the grain boundary. Oxygen K-edge spectra from the bulk and boundary (figure 2(a)) show that there is a change in the ratio of the π^* and σ^* peaks indicating a disruption of the linear titanium-oxygen coordination at the boundary (Brydson et al (1992)). The titanium L-edge spectra (figure 2(b)) however, show there is no shift in the edge onset and no change in either L2/L3 ratio or total L-edge intensity, indicating that the local titanium valence at the boundary is not substantially changed.

3. CONCLUSIONS

Using the Z-contrast image and EELS data, two model grain boundary structural units can be determined that occur in approximately equal numbers; one with TiO columns (figure 3(a)) and the other without (Figure 3(b)), both of which preserve charge neutrality in bond-valence sum calculations. The grain boundary structure itself is composed of an array of these repeating units seperated by the occasional (~every four structural units) $SrTiO_3$ unit. The large number of structural units containing voids indicates that the occupancy of titanium at these sites is very sensitive to the local strain. The voids themselves offer potential sites for accomodation of dopant atoms, which are known to alter the electrical properties of the boundary (Yamaoka et al (1983)). While such an experimental determination obviously does not include relaxation

effects or give the exact location of the atomic columns, it does provide a valuable starting point for theoretical models and in the determination of the relationship between grain boundary structure and bulk properties.

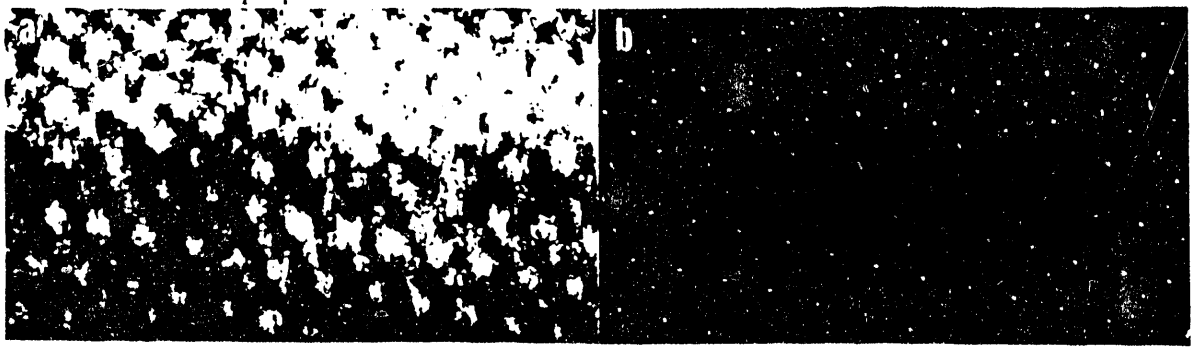

Figure 1: (a) Z-contrast image, (b) maximum entropy processed image

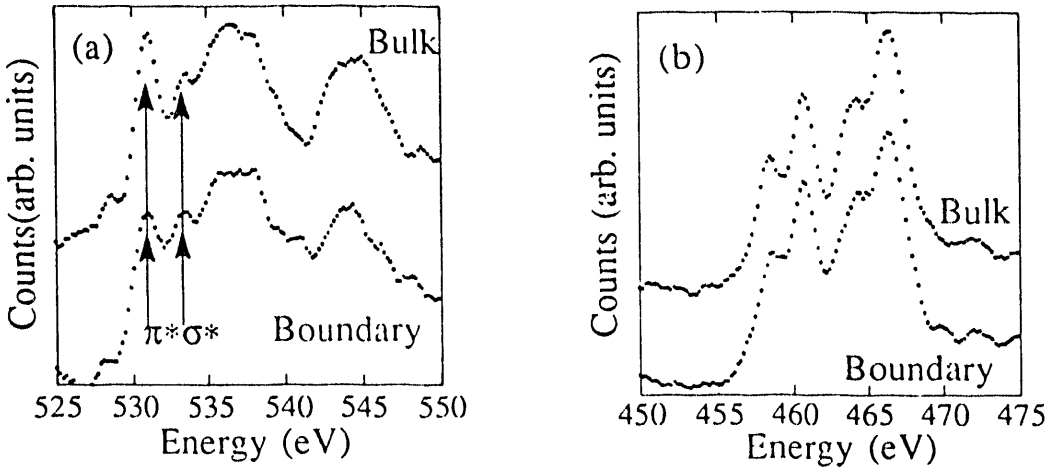

Figure 2: (a) Oxygen K-edges and (b) Titanium L-edges from the bulk and boundary.

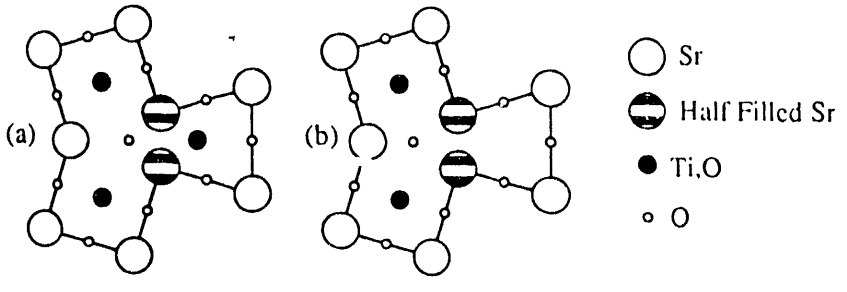

Figure 3: Boundary structural unit with (a) and without (b) TiO columns

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