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ATOMIC RESOLUTION CHARACTERIZATION OF A $SrTiO_3$ GRAIN BOUNDARY IN THE STEM

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High-resolution Z-contrast imaging in the scanning transmission electron microscope (STEM) forms an incoherent image in which changes in atomic structure and composition across an interface can be interpreted intuitively without the need for preconcieved atomic structure models[1]. Since the Z-contrast image is formed by electrons scattered through high angles, parallel detection electron energy loss spectroscopy (PEELS) can be used simultaneously to provide complementary chemical information on an atomic scale [2]. The fine structure in the PEEL spectra can be used to investigate the local electronic structure and the nature of the bonding across the interface [3]. In this paper we use the complimentary techniques of high resolution Z-contrast imaging and PEELS to investigate the atomic structure and chemistry of a 25 degree symmetric tilt boundary in a bicrystal of the electroceramic $SrTiO_3$.

Figure 1(a) shows a Z-contrast image of a symmetric region of the tilt boundary. The brightest spots in the image correspond to the increased scattering power of the Sr atomic columns (Z=38) with the less bright spots corresponding to the Ti atomic columns (Z=22). The lighter O atomic columns are not visible in a Z-contrast image. In figure 1(b) the maximum entropy image processing technique of Gull and Skilling [4] has been applied to enhance the image quality and to determine the positions of the atomic columns in the grain boundary itself. Using the Z-contrast image to position the electron probe, sequences of O K edge and Ti L_{23} edge spectra were acquired at single unit cell intervals across the interface. Figure 2(a) shows a comparison of the O K edge spectra acquired in the bulk and boundary regions of the sample. An increase in the σ^* peak relative to the π^* peak at the grain boundary corresponds to a disruption of the linear O-Ti coordination across the grain boundary [5]. The comparison of the bulk and boundary spectra for the Ti L_{23} edge is shown in figure 2(b). Previous studies of chemical shifts in the PEELS edge energy have observed energy shifts of between 1 and 3eV with a change of valency in transition metals such Ti [6]. Since there is no shift in edge energy observed in figure 2(b) the Ti atoms remain octahedrally coordinated to O across the grain boundary. This is consistent with a constant L_2/L_3 ratio across the grain boundary suggesting that, although distorted, the octahedral Ti coordination is preserved across the grain boundary.

The boundary structure determined from the Z-contrast image above and the PEELS data is shown in figure 3. The grain boundary is composed of two different boundary structural units which occur in approximately equal numbers: one which contains Ti-O columns and the other without. The Ti voids offer potential sites for dopant atoms which are known to significantly effect the electrical properties of these materials. However, the Sr-Sr distance at the base of the triangles in this model structure is only 2.5Å, below the lowest possible nearest neighbor distance for Sr. One possible explanation for the apparent closeness of the Sr columns in the Z-contrast image is that the Sr atoms in these columns lie in alternate planes in the z-direction, giving a Sr-Sr spacing of 4.3Å. This 3 dimensional structure, shown in planar projection in figure 3, is charge-neutral according to bond valence sum calculations.

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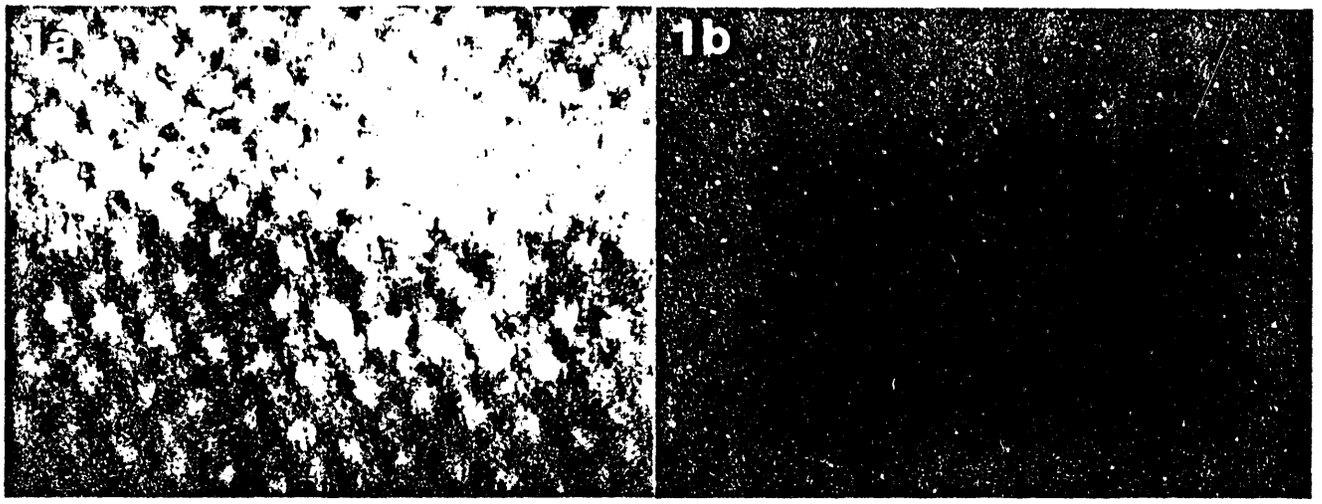

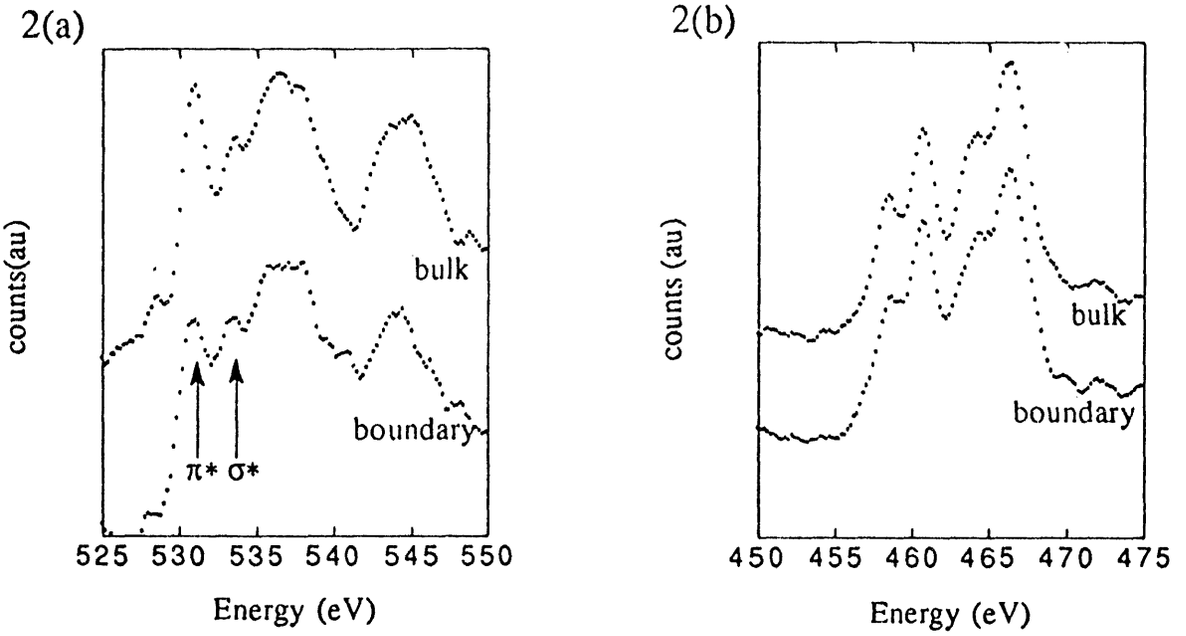

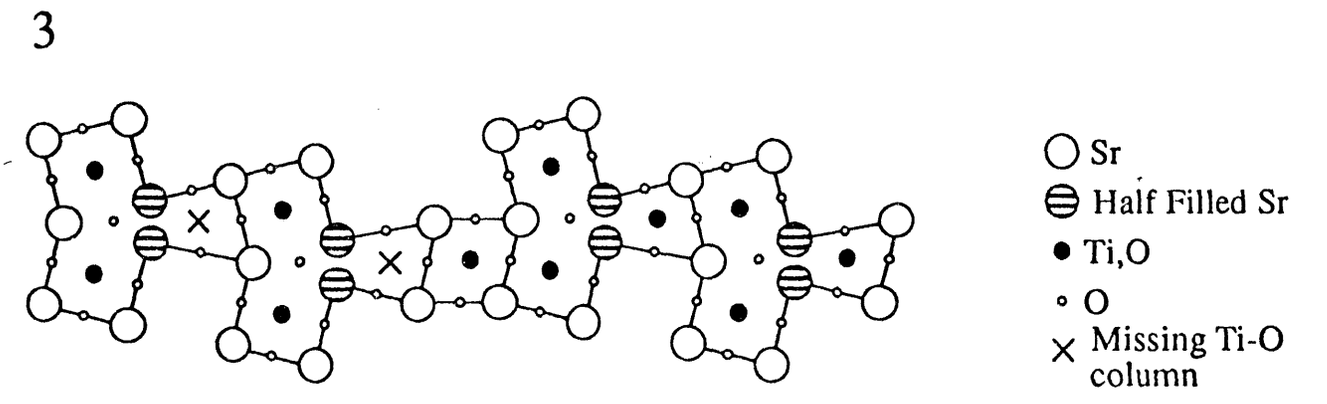

Figure 1: (a) Z-contrast image of a $SrTiO_3$ tilt boundary and (b) maximum entropy processed image.
Figure 2: Comparison of (a) the O K edge spectra and (b) the Ti L_{23} edge spectra from the bulk and boundary regions of the sample.
Figure 3: Grain boundary structure of the $SrTiO_3$ tilt boundary determined from the Z-contrast image and the PEELS data.

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