



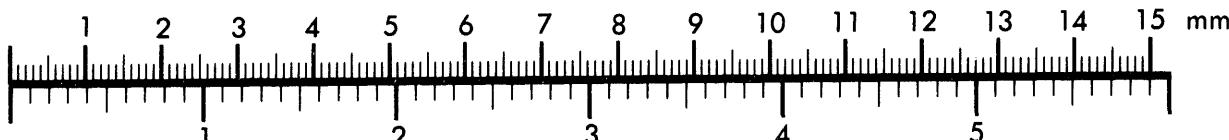
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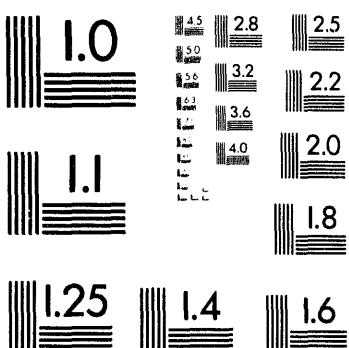
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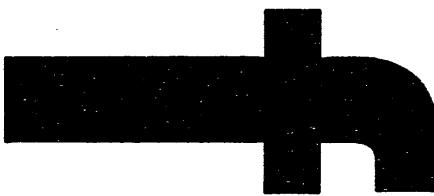
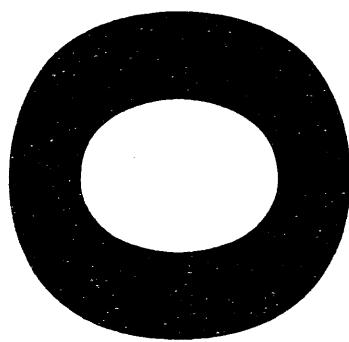


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ATOMIC-RESOLUTION CHARACTERIZATION OF A SrTiO_3 GRAIN BOUNDARY IN THE STEM

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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 preconceived atomic structure models¹. 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 scale². The fine structure in the PEEL spectra can be used to investigate the local electronic structure and the nature of the bonding across the interface³. 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 Skilling⁴ 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 L₂₃ 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 boundary⁵. The comparison of the bulk and boundary spectra for the Ti L₂₃ 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 Ti⁶. 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 L₂/L₃ 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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7. This research was sponsored by the Division of Materials Sciences, US Department of Energy, under contract No. DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc., and supported in part by an appointment to the Oak Ridge National Laboratory Postdoctoral Research Program administered by the Oak Ridge Institute for Science and Education. VR and VPD are supported by U.S. Department of Energy Grant No. DE-FG02-92ER45475.

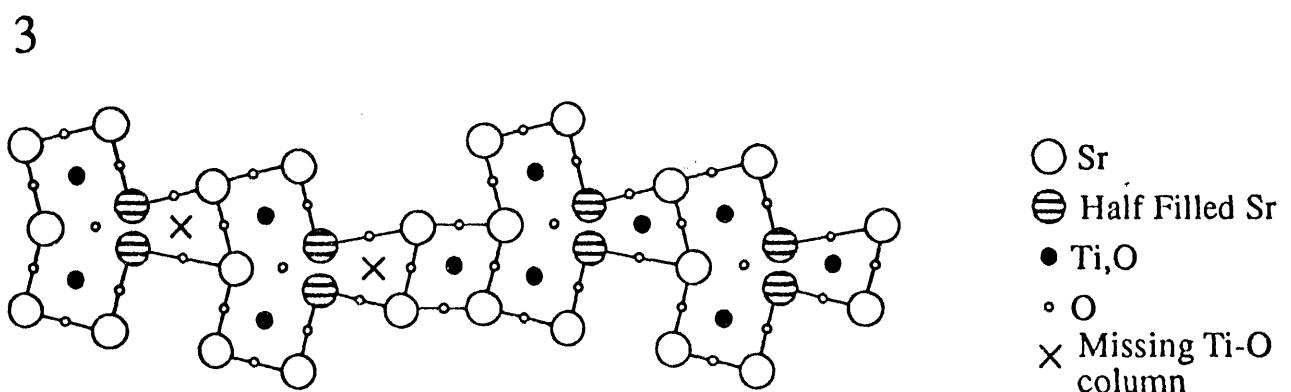
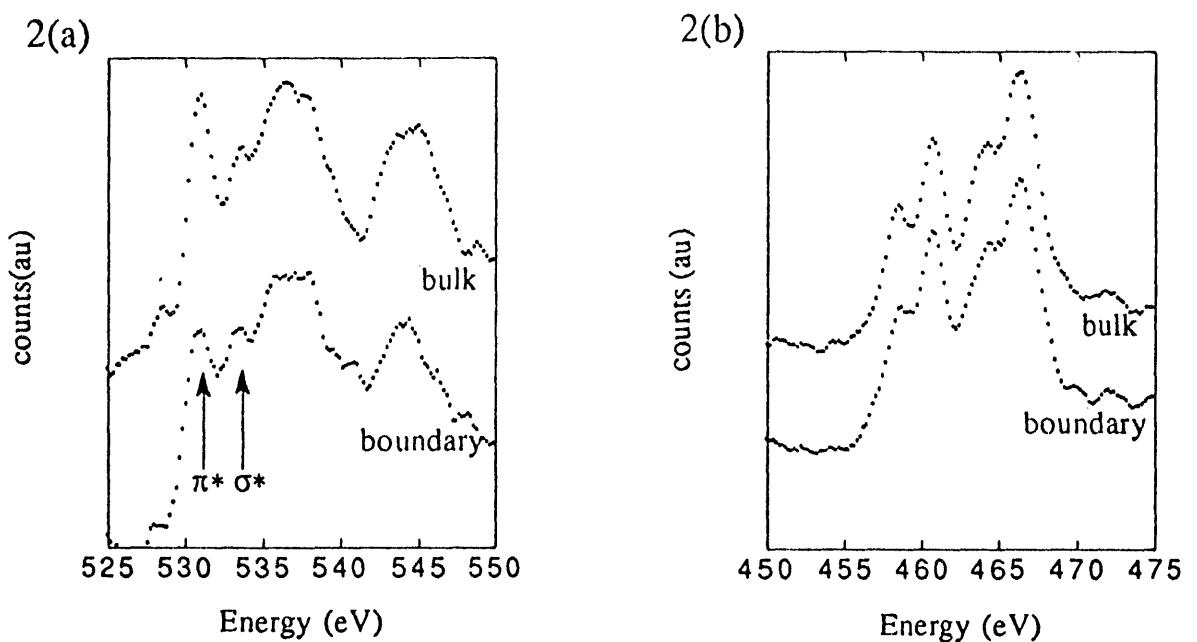
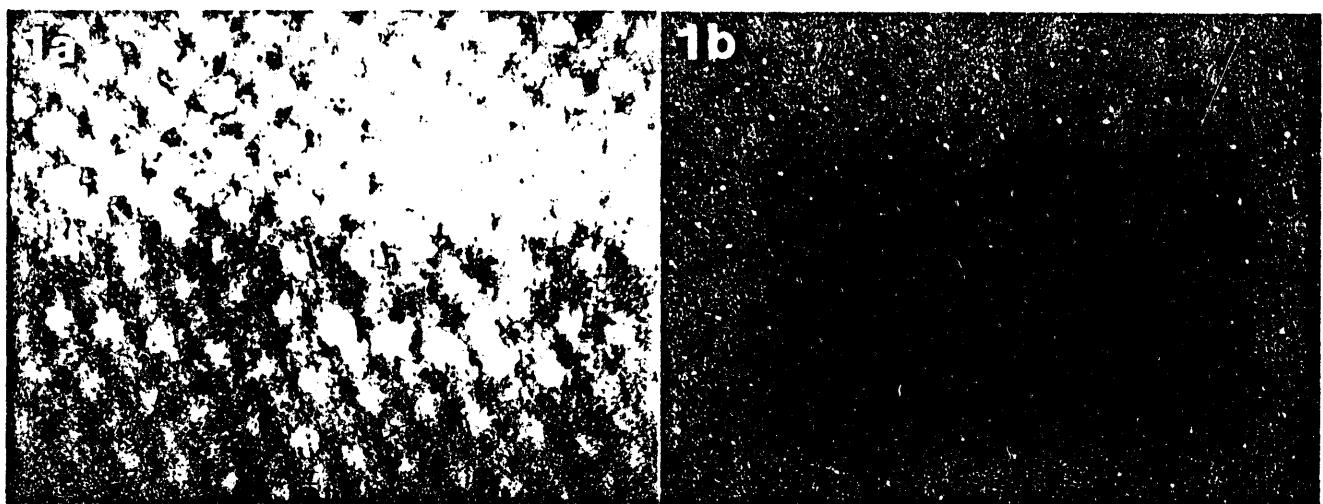


Figure 1: (a) Z-contrast image of a SrTiO_3 tilt boundary and (b) maximum entropy processed image. Figure 2: Comparison of (a) the O K edge spectra and (b) the Ti L₂₃ edge spectra from the bulk and boundary regions of the sample.

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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