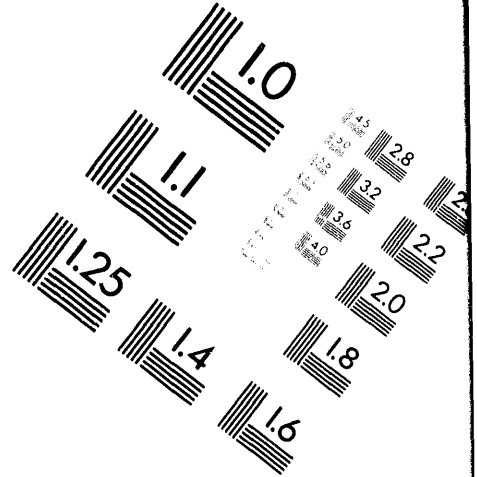
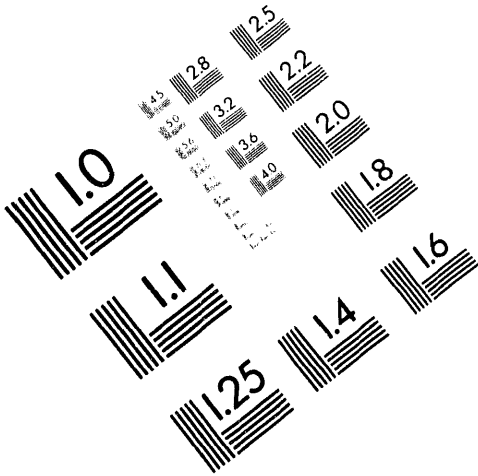




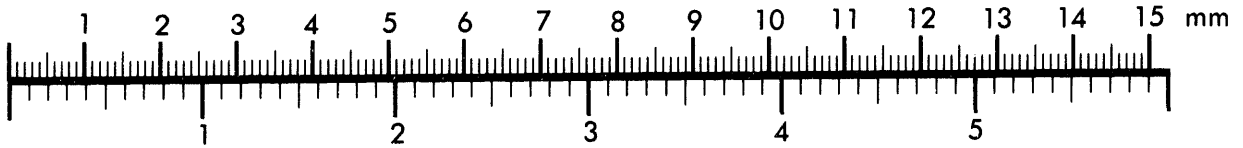
AIM

Association for Information and Image Management

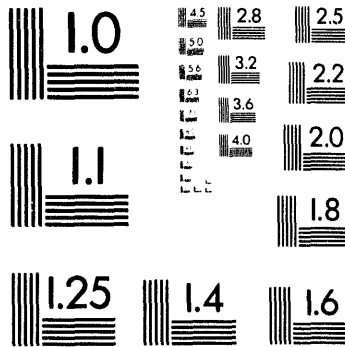
1100 Wayne Avenue, Suite 1100
Silver Spring, Maryland 20910
301/587-8202



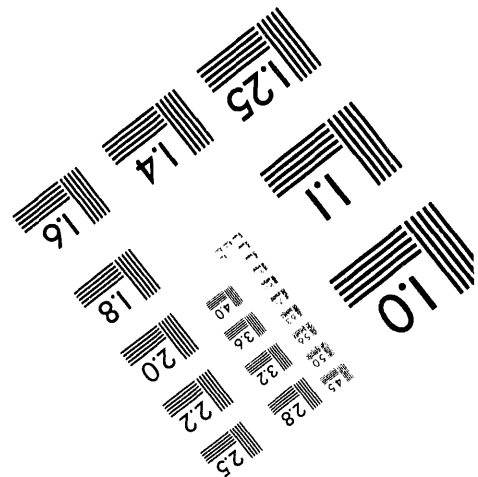
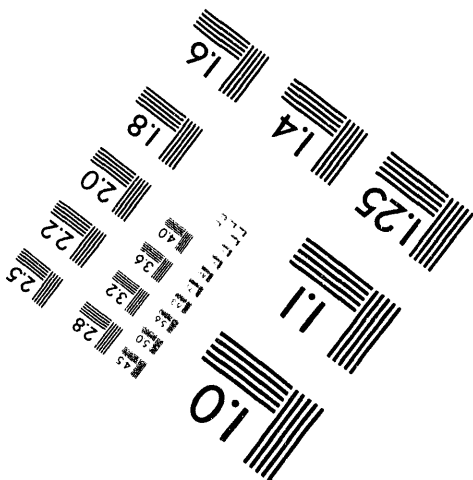
Centimeter

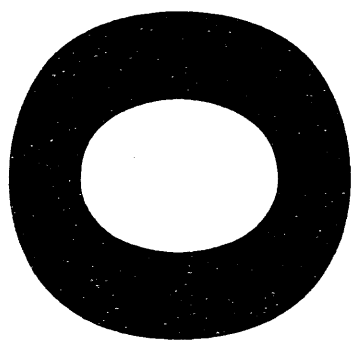


Inches



MANUFACTURED TO AIM STANDARDS
BY APPLIED IMAGE, INC.





Note: This is a preprint of a paper submitted for publication. Contents of this paper should not be quoted or referred to without permission of the author(s).

For publication in
Proceedings of the 52nd Annual Meeting of the Microscopy Society of America, New Orleans, Louisiana, July 31-August 5, 1994

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

M. M. McGibbon, N. D. Browning, M. F. Chisholm, A. J. McGibbon,
S. J. Pennycook, V. Ravikumar,* and V. P. Dravid*

Solid State Division
Oak Ridge National Laboratory
Oak Ridge, Tennessee 37831-6031

*Northwestern University
Department of Materials Science and Engineering
Evanston, IL 60208

"The submitted manuscript has been authored by a contractor of the U.S. Government under contract No. DE-AC05-84OR21400. Accordingly, the U.S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or allow others to do so, for U.S. Government purposes."

SOLID STATE DIVISION
OAK RIDGE NATIONAL LABORATORY
Managed by
MARTIN MARIETTA ENERGY SYSTEMS, INC.
under
Contract No. DE-AC05-84OR21400
with the
U.S. DEPARTMENT OF ENERGY
Oak Ridge, Tennessee

March 1994

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

MASTER

ATOMIC RESOLUTION CHARACTERIZATION OF A SrTiO_3 GRAIN BOUNDARY IN THE STEM

M.M.McGibbon, N.D.Browning, M.F.Chisholm, A.J.McGibbon, S.J.Pennycook, V.Ravikumar* and V.P.David*

Solid State Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831-6031. USA

*Department of Materials science and Engineering, Northwestern University, Evanston, IL 60208

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 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 boundary⁵. 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 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 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.

1. S.J. Pennycook and D.E. Jesson, Ultramicroscopy 37(1991)14

2. N.D.Browning et al, Nature 366(1993)143

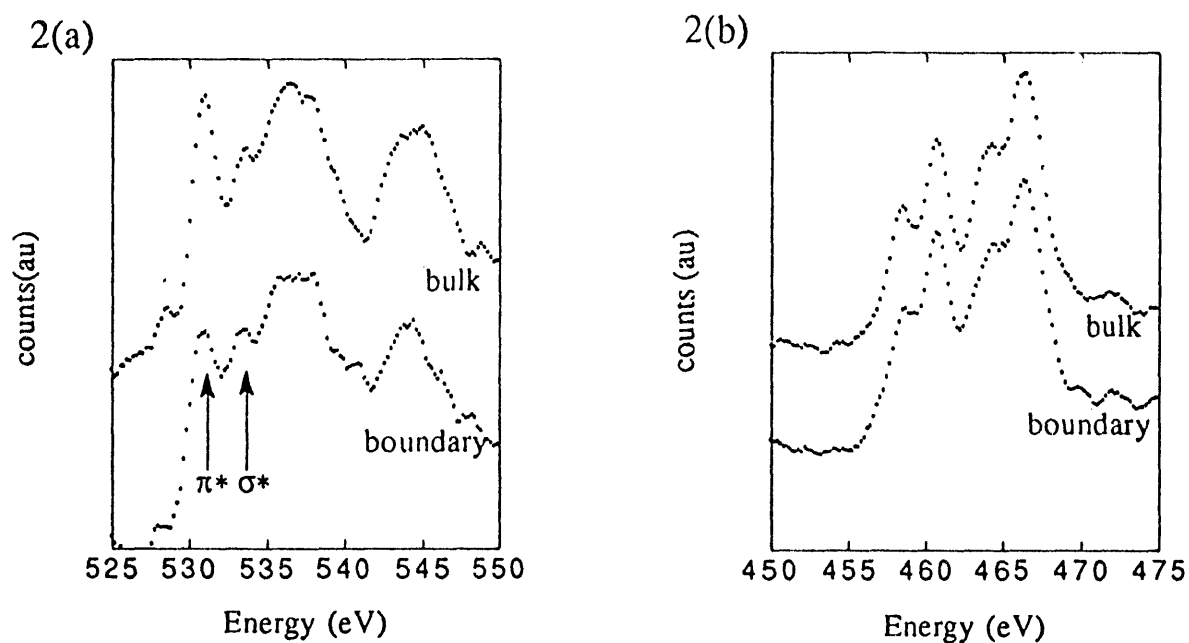
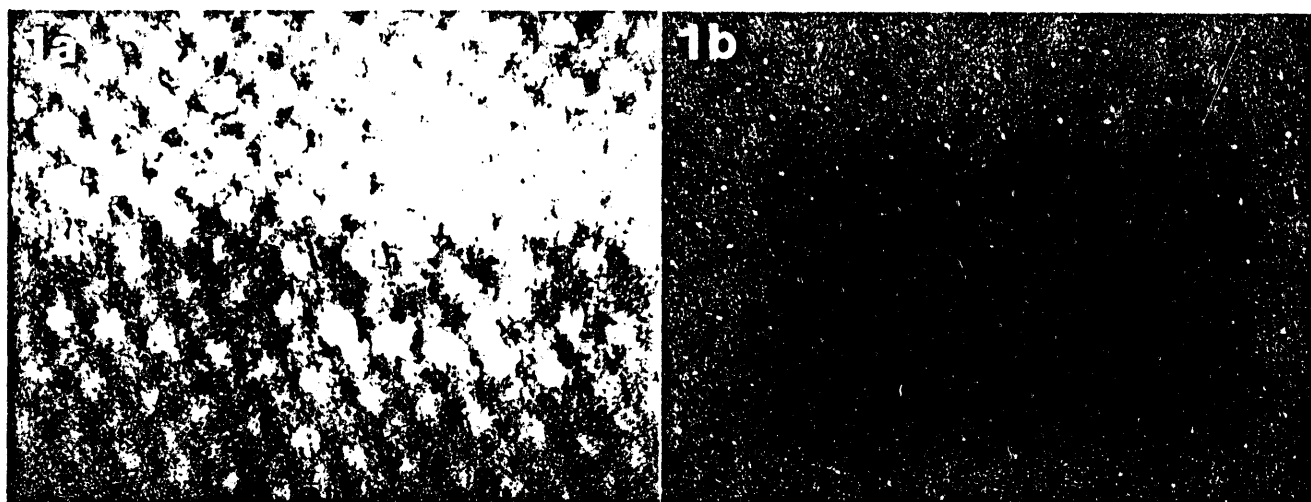
3. P.E.Batson, Nature 366(1993)727

4. S.F.Gull and J.Skilling, IEE Proc 131F(1984)646

5. R.Brydson et al, J.Phys:Condens.Matter 4(1992)3429

6. M.T.Otten et al, Ultramicroscopy 18(1985)285

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.



3

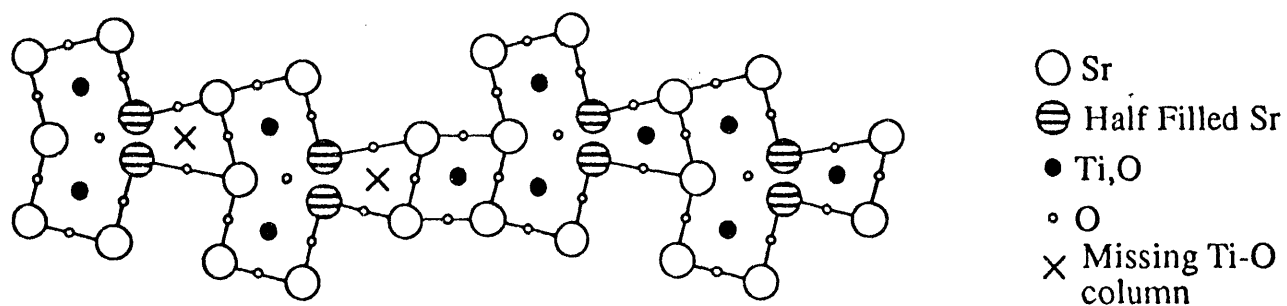


Figure 1: (a) Z-contrast image of a SrTiO_3 tilt boundary and (b) maximum entropy processed image. Figure 2: Comparison of (a) the O K edge spectra and (b) the Ti L_{23} edge spectra from the bulk and boundary regions of the sample. Figure 3: Grain boundary structure of the SrTiO_3 tilt boundary determined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

DATE

FILMED

6/14/94

END

