Direct Atom-Resolved Imaging of Oxides and Their Grain Boundaries
Zaoli Zhang, et al.
Science 302, 846 (2003);
DOI: 10.1126/science.1089785

The following resources related to this article are available online at www.sciencemag.org (this information is current as of February 28, 2007):

Updated information and services, including high-resolution figures, can be found in the online version of this article at:
http://www.sciencemag.org/cgi/content/full/302/5646/846

This article cites 3 articles, 2 of which can be accessed for free:
http://www.sciencemag.org/cgi/content/full/302/5646/846#otherarticles

This article has been cited by 20 article(s) on the ISI Web of Science.

This article has been cited by 1 articles hosted by HighWire Press; see:
http://www.sciencemag.org/cgi/content/full/302/5646/846#otherarticles

This article appears in the following subject collections:
Materials Science
http://www.sciencemag.org/cgi/collection/mat_sci

Information about obtaining reprints of this article or about obtaining permission to reproduce this article in whole or in part can be found at:
http://www.sciencemag.org/help/about/permissions.dtl
also be used to detect DNA sequence polymorphisms and potentially to detect differences in cytosine methylation patterns among Arabidopsis ecotypes, which would be useful for rapid genome-wide mapping of quantitative trait loci (QTL) (42). Finally, WGAs might also be used for direct mapping of point mutations without the use of segregated populations.

The impact of the findings and of the experimental resources developed is not restricted to Arabidopsis. For example, 85% of Arabidopsis genes have close homologs in the rice genome (43). Therefore, this resource will aid in the elucidation of the function(s) of the vast majority of genes in plant genomes (43, 44), providing fundamental knowledge that we hope will eventually lead to the engineering of new plant species.

References and Notes
19. N. Osato et al., Genome Res. 12, 1127 (2002).
21. A large collection of ~20,150 RIKEN Arabidopsis full-length (RAFL)-cDNAs were produced by the RIKEN Genome Sciences Center (21) and the complete sequence of the majority of RAFLs was determined in this study [fig. 52; (22)].
22. Materials and Methods are available as supporting material on Science Online.
23. A collection of ~2300 full-cDNAs have been constructed by various laboratories known as the CFLs (community full length) whose construction proceeded the two large full-cDNA collections (22).
34. P. Carninci et al., Genomics 77, 79 (2001).
35. The majority of ORF clones (7875) were constructed by transferring the ORFs from the RAFL clones into the pUN151 cloning vector (45). The remaining 875 ORFs consisted of 594 chip-derived RT-PCR clones produced to replace defective RAFL clones and ORF clones for 282 new ANE genes. The ORF PCR products were subcloned as SfiA/SfiB fragments (fig. S18), allowing unidirectionality of the cloning process.
42. J. O. Borevitz et al., Genome Res. 13, 513 (2003).
43. S. A. Goff et al., Science 296, 92 (2002).
46. The distribution of the various types of full-cDNAs that correspond to genes with the same or different annotated gene structure is as follows: same annotated structure, CFl 20%; Cers, 33%; RAFl 43%; C-clones, 3%; different annotated structure, CFl 10%; Cers, 27%; RAFl 61%.
47. We thank M. Johnston for critical reading of the manuscript, K. Mayer for gene functional category information, and T. Gingeras for support of this project. We also thank S. Elledge for providing us with the pUN150 vector and P. Surko, J. Borevitz, and T. Mockler for useful discussions. Supported by the NSF Plant Genome Research Program under awards DBI-9975718, DBI-0106908 (to J.R.E.), DBI-9878275 (to R.W.D.), and USDA CRIS no. 5335-21430-005-00D (to A.T.). This study has also been supported by Research Grant for Genome Research from RIKEN (to K.S.) and by Research Grant for the RIKEN Genome Exploration Research Project from the Ministry of Education, Culture, Sports, Science and Technology of the Japanese Government (to Y.H.). Affymetrix gene tile array expression data have been deposited in the Gene Expression Omnibus (GEO) database (www.ncbi.nlm.nih.gov/geo/). Accession numbers are as follows: pilot tile arrays, GSM9899 through GSM9101 and GSM9196 through GSM9207; whole genome arrays, GSM9842 through GSM9877 and GSM9208 through GSM9219. GEO accessions for pilot and whole genome array analysis files: GSM601, GSE636–639. GenBank accession numbers can be found on table S6.

Supporting Online Material
www.sciencemag.org/cgi/content/full/302/5646/842/DC1
Materials and Methods
SOM Text
Figs. S1 to S27
Tables S1 to S6
References
23 June 2003; accepted 10 September 2003

Direct Atom-Resolved Imaging of Oxides and Their Grain Boundaries
Zaoli Zhang, Wilfried Sigle, Fritz Philipp, Manfred Rühle*

Using high-resolution transmission electron microscopy, we obtained structure images of strontium titanate (SrTiO3) with a clearly resolved oxygen sublattice along different crystallographic directions in the bulk lattice and for a 2.3-tilt grain boundary. Comparison with image simulations showed that the grain boundary contains oxygen vacancies. Measurements of atom displacements near the grain boundary revealed close correspondence with theoretical calculations.

Direct imaging of atoms in oxides, especially in defect regions, is of considerable importance for understanding the properties of materials. Because oxygen has a high electronegativity, its presence can have a marked effect on these properties. This can occur through the binding of free electrons, which leads to a loss of electrical conductivity (e.g., in metal oxides) through the presence of vacancies in the oxygen sublattice, which in turn can give rise to considerable ionic conductivity (as in electroceramic materials).

Oxygen has a strong effect on mechanical properties, which are directly linked with the strong interatomic forces. But oxygen can also have an indirect influence: Most properties of materials are sensitively influenced by the presence of crystal defects, and the oxygen concentration at such defects can drastically deviate from the average bulk value, even in thermal equilibrium. This is one of the reasons why grain boundaries (GBs) in electroceramics can be electrically charged and form a double Schottky barrier against the movement of ions (1, 2), which is of ultimate importance in polycrystalline electroceramic materials. Recently, it was shown that dislocations in SrTiO3 can be oxygen deficient (3) and that this can lead to a change

Max-Planck-Institut für Metallforschung, Heisenbergstraße 3, D-70569 Stuttgart, Germany.

*To whom correspondence should be addressed. E-mail: ruehle@mf.mpg.de

www.sciencemag.org

Published by AAAS
in the dislocation core structure (4), which in turn may affect the mechanical properties of the material substantially (5).

These examples show that the determination of the atomic structure of oxides, and in particular the determination of defects in oxides, is critical for an understanding of their material behavior. For the past 15 years, the high-resolution transmission electron microscope (HRTEM) has been the most appropriate tool for the direct imaging of the atomic structure of materials. This is possible because the point-to-point resolution of modern TEMs has reached the regime of subinteratomic distances. However, a general problem occurs if atoms with low atomic number Z, such as oxygen, are to be imaged because they only weakly scatter electrons. This is particularly true if these atoms are surrounded by atoms of much higher Z, which is the case in most oxides. Recent breakthroughs were achieved by exit-wave reconstruction (6) and particularly with the advent of the spherical aberration–corrected HRTEM (7). Direct imaging of the oxygen sublattice in oxides has been shown to be feasible, but the structure of the oxygen sublattice in the vicinity of crystal defects has not yet been explored. Here, we used the Stuttgart JEOL ARM1250 high-voltage TEM with a point-to-point resolution of 0.12 nm and an information limit of 0.11 nm (8) to demonstrate oxygen imaging both in the bulk and at a GB in SrTiO₃. Images were taken at or close to Scherzer defocus, which for this type of microscope is optimum because strong oscillations of the contrast function are avoided (resulting in easy-to-interpret structure images) while contrast delocalization is kept to close minimum.

For the single-crystal experiments we used (110)-, (111)-, and (001)-orientated crystals (Crystal GmbH, Berlin). A Σ3{111}{110} tilt GB was manufactured by diffusion bonding in ultrahigh vacuum (9) of two undoped SrTiO₃ crystal platelets (Crystal GmbH). For the bicrystal, we prepared TEM specimens for observation along a [110] direction. First, we cut 3-mm disks normal to [110] with a GB passing through the disk center. After mechanical grinding to about 100 μm and subsequent dimple grinding to about 20 μm, a final ion-beam milling with Ar⁺ ions from both sides was performed. For ion milling, an inclination angle of 12° was used. The ion energy was 3 keV in a Gatan Duomill (Gatan Inc., Pleasanton, CA).

Figure 1 shows HRTEM images taken along all three low-index directions: [110], [111], and [100]. An image taken from bulk area in SrTiO₃ at an underfocus of 75 nm is shown in Fig. 1A. The crystal is oriented parallel to the [110] direction. Along this direction, the [100] planes show an ABAB stacking sequence, with A-type planes composed of alternating Ti and O columns and B-type planes composed of mixed Sr-O columns. Sr-O columns show strong bright contrast under these imaging conditions. Within the A-type planes there are clear contrast maxima at the sites of Ti and O columns. The spacing between Ti and O columns is 0.138 nm, which is well above the spatial resolution of the microscope. To prove that these contrast variations are due to the presence of oxygen, we performed HRTEM image simulations using the multislice method within the EMS software package (10). The structure model and the simulated image (Fig. 1A, insets) show close correspondence with the experimental image. We removed the oxygen atoms from one of the O columns (arrow in Fig. 1A), which leads to a noticeable change of the image contrast.

Along the [111] direction, mixed Sr-Ti columns exist around which there are six O columns forming a hexagon. The separations between the O columns and their neighboring Sr-Ti and O columns are both 0.159 nm. An image taken at an underfocus between 25 and 35 nm is shown in Fig. 1B. The image was taken from a thin area where Sr-Ti columns are imaged by dark contrast while O columns are imaged by bright contrast. The simulated image at an underfocus of 25 nm and specimen thickness of 2.0 nm (inset, lower right) reveals that the contrast is identical to that of the experimental image.

Along the [100] direction, the Ti-O columns are surrounded by four O columns. The separations between the O columns and their neighboring Ti-O and pure Sr columns are both 0.195 nm. In a HRTEM image recorded at an underfocus of 85 nm (Fig. 1C), Sr, Ti-O, and O columns appear with bright contrast, with the O contrast the strongest. The calculated image based on the atomic model (inset, lower right) is consistent with the experimental image.

Next, a Σ3{111}{110} tilt GB was investigated close to Scherzer defocus (−34 nm). From the image (Fig. 2A), Sr-O, Ti, and O columns are resolved not only in the bulk regions remote from the boundary but also at the GB itself. The contrast features along the GB are separated by about 0.24 nm, which shows that the GB plane consists of Sr-O and O columns. If it consisted of Ti columns, the separation of the contrast features would be twice as large. The intensity profile along the GB plane (Fig. 2A, inset) shows that the intensities at the O columns are not constant. One column that exhibits exceptionally strong brightness is marked by a white arrow. This might imply that the occupancy of this atom column is less than unity. To quantify the results, we constructed a coincidence site lattice (CSL) model of the Σ3{111}{110} GB (Fig. 2B). Within this model, we removed half of the oxygen atoms from one O column in the GB (indicated by an arrow). Image simulations were performed using the multislice method within EMS. The thickness-defocus map reveals that variations of the specimen thickness between 3.5 and 8 nm and underfocus values between 40 and 50 nm did not substantially change the image con-
The index $n$ stands for the distance from the boundary, where $n = \pm 1$ is closest to the GB. We calculated average values for all $\delta_n$ with $n \neq 1$ (i.e., the bulk values) and plotted differences with respect to these average values in Fig. 3, A to C. We found that the spacings $\delta_{1}^{Ti}$, $\delta_{1}^{Sr}$, $\delta_{1}^{C}$, and $\delta_{1}^{O}$ are different from the average values (12). Relative to the bulk values, $\delta_{1}^{Ti}$ is lower by 0.026 ± 0.007 nm, whereas $\delta_{1}^{Sr}$ is higher by 0.033 ± 0.007 nm. These results show that the atom columns are not located at the positions of the CSL model, but have undergone relaxation. The separation of the two close Ti atom columns facing each other at the GB is increased by 0.052 nm as a consequence of their positive charges. The separation of the two closest Sr-O columns facing each other at the GB is decreased by 0.066 nm.

In addition, the $\delta_{1}^{C}$ and $\delta_{1}^{O}$ values are higher, which means that the first spacing is larger relative to the bulk value. This reveals that the GB is expanded. The observed differences of the spacings are 0.022 ± 0.005 nm for the upper crystal and 0.021 ± 0.006 nm for the lower crystal. Thus, the resultant GB expansion is 0.043 ± 0.008 nm. To exclude imaging artifacts, we did the same measurements in the simulated image of the CSL model. The solid symbols in Fig. 3C show that for this model no variation of the atom column separations occurs, which means that the observed variations are directly related to the real atomic structure. These results coincide well with density functional calculations (13), which show an increase of the Ti atom column separations by 0.038 nm and a decrease of the Sr-O column separations by 0.054 nm. An average expansion of 0.061 ± 0.009 nm normal to the boundary plane was also detected by the refinement procedure (14). It is possible that the small differences between experimental and ab initio results are related to the presence of oxygen vacancies at the GB. The spacing closest to the GB is larger, which corresponds to an increased separation of the two Sr columns facing each other at the GB. The separation of the two close Ti atom columns facing each other at the GB is increased by 0.052 nm as a consequence of their positive charges. The separation of the two closest Sr-O columns facing each other at the GB is decreased by 0.066 nm.

The arrow shows the position of the half-occupied O structure model in (B) (underfocus, 50 nm; thickness, 4.2 nm). The intensity profile along the GB, in which the O column marked by an arrow shows reduced occupancy. Inset: Intensity profile along the GB, in which the O column is the second atom column (denoted $\delta_1$), between subsequent Ti atom columns facing each other at the GB. The separation of the two close Ti atom columns facing each other at the GB is increased by 0.052 nm as a consequence of their positive charges. The separation of the two closest Sr-O columns facing each other at the GB is decreased by 0.066 nm.

Perpendicular to the GB we measured spacings (see Fig. 2B) between subsequent Ti atom columns (denoted $\delta_1$), between subsequent Sr-O atom columns ($\delta_2$), and between Sr-O atom columns at the CSL positions ($\delta_3$).

The index $n$ stands for the distance from the boundary, where $n = \pm 1$ is closest to the GB. We calculated average values for all $\delta_n$ with $n \neq 1$ (i.e., the bulk values) and plotted differences with respect to these average values in Fig. 3, A to C. We found that the spacings $\delta_1^{Ti}$, $\delta_1^{Sr}$, $\delta_1^{C}$, and $\delta_1^{O}$ are different from the average values (12). Relative to the bulk values, $\delta_1^{Ti}$ is lower by 0.026 ± 0.007 nm, whereas $\delta_1^{Sr}$ is higher by 0.033 ± 0.007 nm. These results show that the atom columns are not located at the positions of the CSL model, but have undergone relaxation. The separation of the two close Ti atom columns facing each other at the GB is increased by 0.052 nm as a consequence of their positive charges. The separation of the two closest Sr-O columns facing each other at the GB is decreased by 0.066 nm.

In addition, the $\delta_1^{C}$ and $\delta_1^{O}$ values are higher, which means that the first spacing is larger relative to the bulk value. This reveals that the GB is expanded. The observed differences of the spacings are 0.022 ± 0.005 nm for the upper crystal and 0.021 ± 0.006 nm for the lower crystal. Thus, the resultant GB expansion is 0.043 ± 0.008 nm. To exclude imaging artifacts, we did the same measurements in the simulated image of the CSL model. The solid symbols in Fig. 3C show that for this model no variation of the atom column separations occurs, which means that the observed variations are directly related to the real atomic structure. These results coincide well with density functional calculations (13), which show an increase of the Ti atom column separations by 0.038 nm and a decrease of the Sr-O column separations by 0.054 nm. An average expansion of 0.061 ± 0.009 nm normal to the boundary plane was also detected by the refinement procedure (14). It is possible that the small differences between experimental and ab initio results are related to the presence of oxygen vacancies at the GB. The spacing closest to the GB is larger, which corresponds to an increased separation of the two Sr columns facing each other at the GB. The separation of the two close Ti atom columns facing each other at the GB is increased by 0.052 nm as a consequence of their positive charges. The separation of the two closest Sr-O columns facing each other at the GB is decreased by 0.066 nm.

The arrow shows the position of the half-occupied O structure model in (B) (underfocus, 50 nm; thickness, 4.2 nm). The intensity profile along the GB, in which the O column marked by an arrow shows reduced occupancy. Inset: Intensity profile along the GB, in which the O column is the second atom column (denoted $\delta_1$), between subsequent Ti atom columns facing each other at the GB. The separation of the two close Ti atom columns facing each other at the GB is increased by 0.052 nm as a consequence of their positive charges. The separation of the two closest Sr-O columns facing each other at the GB is decreased by 0.066 nm.
the GB that were not considered in the theoretical studies. The presence of oxygen vacancies would remove negative charge from the area between the close Ti atom columns and thus increase the Ti-Ti distance, as found in our experiment.

We have shown how HRTEM can be used for direct imaging of the oxygen sublattice near a crystal defect in SrTiO3 at atomic resolution. In addition to this structural information, a quantitative comparison with simulated HRTEM images should enable determination of the local chemical composition of oxides on the atomic scale. Our results strongly indicate that it should also be possible to resolve light elements in nonoxide materials such as borides, nitrides, or carbides. This would be of central importance for the understanding of defects in these materials.

References and Notes

11. The experimental image presented here was obtained from digital charge-coupled device camera recordings of the original negative films. It can grab image pixels from an area of 1536 × 1024 pixels at a spatial sampling rate of 0.013 mm/pixel. The displacement analysis was done in the negative image with DigitalMicrograph 3.6 (Gatan).

For $T_g$ and $T_T$ we only measured the spacing in the upper crystal because the contrast is more homogeneous in this part of the image. For $T_T$ we measured spacings from both the upper and lower crystals. The error bars correspond to the standard deviation determined from the statistical average.

14. We thank U. Salzberger for excellent TEM specimen preparation, R. Höschen for his help during the operation of the ABM1250, and C. T. Koch and G. Richter for helpful discussions with the image simulations.

29 July 2003; accepted 25 September 2003

Is the Fragility of a Liquid Embedded in the Properties of Its Glass?

Tullio Scopigno, Giancarlo Ruocco, Francesco Sette, Giulio Monaco

When a liquid is cooled below its melting temperature, it usually crystallizes. However, if the quenching rate is fast enough, the system may remain in a disordered state, progressively losing its fluidity upon further cooling. When the time needed for the rearrangement of the local atomic structure reaches approximately 100 seconds, the system becomes "solid" for any practical purpose, and this defines the glass transition temperature $T_g$. Approaching this transition from the liquid side, different systems show qualitatively different temperature dependencies of the viscosity, and accordingly they have been classified by introducing the concept of "fragility." We report experimental observations that relate the microscopic properties of the glass phase to the fragility. We find that the vibrational properties of the glass well below $T_g$ are correlated with the fragility value. Consequently, we extend the fragility concept to the glassy state and indicate how to determine the fragility uniquely from glass properties well below $T_g$.

When a liquid is cooled, the loss of kinetic energy leads to an ordering of the molecules, which then crystallize at the melting temperature $T_m$. However, if cooled fast enough through $T_m$, some materials (glass-forming materials) are capable of sustaining a metastable liquid state and, upon further cooling, of freezing into a disordered glassy state (1–4). The law that describes the change of the viscosity with the temperature approaching the glass transition temperature, $T_g$, is highly material-specific and has led to the classification of glass-forming materials according to the concept of "fragility" (5, 6). The kinetic fragility, $m$, is directly related to the slowing down of the dynamics: It is defined in terms of the shear viscosity $\eta$ as

$$m = \lim_{T \to T_g} \frac{d \log(\eta)}{d (T_g/T)}$$

Therefore, $m$ is an index of how fast the viscosity increases while approaching the structural arrest at $T_g$, the temperature at which the structural relaxation time $\tau_{(s)} \sim 100$ s. At this latter temperature, through the Maxwell relation $\eta = G_\tau \pi$, one finds a viscosity of $\eta \sim 10^{13}$ poise (more likely, $\eta \sim 10^{14}$ poise for molecular glasses), whereas $10^{-4}$ poise is the "infinite" temperature limit in basically any material. Consequently, fragility values typically range between $m = 17$ for "strong" systems (those that show an Arrhenius behavior) and $m \sim 150$ for "fragile" systems, where the high cooperativity of the diffusive dynamics induces a high (and $T$-dependent) apparent activation energy. One interesting element of this classification lies in the attempt to relate the temperature behavior of a macroscopic transport property close to $T_g$ to the microscopic interactions driving the dynamics of the system. It has been found, for example, that the value of the fragility is empirically related to the kind of interaction potential among the particles constituting the system. Prototypical examples of fragile liquids are those composed by units interacting via isotropic bonds, such as van der Waals-like molecular liquids. The strong glass-forming liquids, on the other hand, are those characterized by strong covalent directional bonds that form space-filling networks. $O$-terphenyl ($m = 80$) and SiO$_2$ ($m = 20$) are characteristic examples of a fragile and a strong liquid, respectively. Hydrogen-bonded systems, such as glycerol ($m = 50$), are often called "intermediate" between strong and fragile liquids. Kinetic fragility has been found to be correlated to other properties of the glass-forming liquids, such as (i) the slope at $T_g$ of the temperature dependence of the configurational entropy (often referred to as thermodynamic fragility) (7) (or for classes of systems sharing similar $T_g$'s) the specific heat jump at $T_g$ (8, 9); (ii) the ratio between the maximum and the minimum of the boson peak; that is, of the bump observed at terahertz frequencies in the Raman and neutron-scattering spectra of glass-forming materials (10) [although this finding is controversial (11)]; (iii) the degree of stretching in the non-exponential decay of the correlation functions in the liquid close to $T_g$ (12); (iv) the statistics of the minima in a potential energy landscape-based description (13, 14) of the diffusion process in supercooled liquids (15–17); and, more recently, (v) the temperature behavior of the shear elastic modulus in the supercooled liquid (18). In all these studies, the fragility has been always related to (or defined through) macroscopic properties characterizing the liquid side of the glass transition. Although there are attempts to relate the fragility to the anharmonicity of the "hot" glass (19), no connection has been found up to now between the...