

Electrostatic fields control grain boundary structure in SrTiO₃

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Abstract: Functional properties of oxide ceramics are often controlled by the addition of dopant elements and the resulting alteration of oxygen vacancy concentrations within grain boundary core structures. A challenge in designing nanoscale ceramic microstructures is forming stable grain boundary networks, while minimizing unwanted impurity concentrations. In this study, it was discovered that the application of electrostatic fields during diffusion bonding of undoped SrTiO₃ bicrystals leads to modifications of grain boundary core structures while misorientation angles remained unchanged. The applied electric field not only changes atomic and electronic interface structures, but also causes modifications of ensuing dielectric properties by altering local oxygen vacancy concentrations. The observations for this model system demonstrate the potential to control and modify the microscopic degrees of freedom of grain boundaries in the absence of dopant elements. Field-assisted modifications of grain boundary networks may become a disruptive technology in designing oxide microstructures for a wide range of applications.

Success in controlling the unique physical properties of nanocrystalline ceramics, which exhibit an increased number of grain boundaries per unit volume, requires application of appropriate methods to manipulate the atomic configuration and chemical composition of interface structures.¹ In electroceramics, such as perovskite oxides, the macroscopic physical properties are typically controlled by interfacial oxygen vacancies along with the respective

mechanisms that maintain charge balances, affecting polarization.^{2,3} The addition of dopant elements and their segregation to grain boundaries is an efficient tool to modify grain boundary configurations as well as control densification behavior and grain growth.⁴ Electric field assisted sintering techniques, which include spark plasma sintering and flash sintering, have recently demonstrated enhanced densification in ceramic oxides.⁵ To date, the effect of electric fields on grain boundary structures remains unclear. The application of an electric field to single crystalline SrTiO₃, which serves as a model for oxide ceramics in this study, is shown to induce a redistribution of oxygen anions and vacancies as well as alter surface configurations.⁶⁻⁸ This effect enables the ability to control oxygen vacancy distributions by switching the polarity of the electric field. However, the surface structure was found to reverse to its initial configuration once the applied field is removed.^{7,9,10} This study demonstrates that application of an electrostatic field during diffusion bonding of SrTiO₃ bicrystals with a (100) twist grain boundary results in the formation of atomic and electronic grain boundary core structures that are distinctly different from grain boundaries with the same disorientation but bonded in the absence of an applied electric field.

SrTiO₃ bicrystals were formed with a nominal twist angle of 41° by joining two polished (100) surfaces of SrTiO₃ single crystals (MTI Corporation) with a relative rotation about their common [100] axis. Cleaning and etching procedures for the single crystal surfaces prior to diffusion bonding are detailed elsewhere.¹¹ Diffusion bonding was performed in air at 1480°C for 210 minutes under a uniaxial pressure of 6 MPa along the interface normal. A heating rate of 350°C/hr and a cooling rate of 120°C/hr was used for all samples to ensure consistency in defect concentration associated with heating and cooling rates.¹² During diffusion bonding an electric bias of either 0 V or 30 V was applied, corresponding to an electric field strength of 0 V/cm or

10 V/cm across the grain boundary core, and along the normal of the boundary plane (see Figure 1). After diffusion bonding, Transmission Kikuchi Diffraction (TKD) experiments revealed misorientation angles between adjacent half-crystals ranging between 39.5° and 42.1° . Samples for cross-sectional transmission electron microscopy (TEM) characterization were prepared using a FEI Scios dual-beam focused ion beam (FIB) instrument. After FIB sectioning low voltage Ar^+ ion milling was performed with a Fischione Nanomill initially at 900 eV and subsequently at 500 eV to reduce ion beam damage. Atomic grain boundary core structures were characterized by high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) imaging. The probe-forming convergence semi-angle was 23.4 mrad and the inner-detector semi-angle was approximately 77 mrad. Electron energy-loss spectroscopy (EELS) was used to assess changes in the energy-loss near-edge fine structure (ELNES) of the Ti $L_{2,3}$ and O K absorption edges across respective grain boundary planes. The collection semi-angle for EELS measurements was less than 15 mrad. ELNES represents local symmetry-projected unoccupied densities of states and was used to ascertain local interfacial bonding configurations. HAADF-STEM and EELS experiments were carried out with an aberration-corrected JEOL JEM2100F STEM instrument operating at 200 kV. Impedance spectroscopy for investigated bicrystals was performed with a Novocontrol Alpha-A impedance analyzer using an applied AC voltage of 40 mV over a frequency range of 10 Hz-10 MHz. Tests were conducted at room temperature in a dry ambient environment with Au or Au/Pd electrodes. Capacitance data was corrected for sample geometry.

Figure 2 shows HAADF-STEM micrographs of the grain boundary core structures for bicrystals formed in the presence ('EF bicrystal') and in the absence of an applied electric field ('noEF bicrystal'). Each boundary is observed edge-on in two different zone-axis orientations.

Examination of the interface structures with one half-crystal oriented along either the [100] or the [110] zone-axis reveals a grain boundary core width, i.e., interface expansion, of only 0.43 ± 0.03 nm for EF bicrystals (Figures 2a and 2b). A significantly larger interface expansion of 0.89 ± 0.13 nm was observed for noEF bicrystals (Figure 2c and 2d). Both grain boundary configurations are atomically structured and periodic over extended distances along the grain boundary planes. No secondary phases or intergranular films were observed. The HAADF intensities in Figure 2a and 2b indicate that the core of the EF bicrystal is composed of a singular row of Ti ions. The noEF bicrystals exhibit a more complex structural arrangement with an overall reduced HAADF intensity, likely arising from altered electron channeling conditions.¹³ The atomic grain boundary core structure of the noEF bicrystals is remarkably similar to reconstructions previously observed for free (100) surfaces of SrTiO₃.¹⁴ The bicrystals displayed in Figure 2 were diffusion bonded under identical experimental conditions except for the applied electric field strength. It is therefore concluded that the observed modifications of the atomic interface structure arise from the electric field applied during diffusion bonding.

Spatially resolved ELNES of the Ti L_{2,3} and O K edges were acquired with one of the half crystals close to <100> zone-axis orientation. In bulk SrTiO₃, Ti L_{2,3} edges exhibit a crystal field splitting of ~ 2.2 eV between unoccupied Ti 3d e_g and t_{2g} electron states, while the O-K edge exhibits four major peaks reflecting local O 2p hybridization with unoccupied Ti 3d states.^{15,16} Figure 3 and 4 show representative background-stripped ELNES for the EF bicrystals and noEF bicrystals, respectively. Spectra recorded from each side but several nanometers away from the grain boundary cores were indistinguishable from each other, and are in good agreement with those previously observed from bulk SrTiO₃.¹⁷ This result demonstrates that crystal orientation, i.e., electron channeling effects, were negligible during EELS acquisition. Within the grain

boundary core regions, changes in the ELNES signatures are confined to 1.2 nm (i.e., 3 unit cells) and 2.0 nm (5 unit cells) for EF bicrystals and noEF bicrystals, respectively. Similar to the observed atomic structures (Figure 2), interfacial electronic structures of the EF bicrystals extend over a smaller interval across the interface plane compared to the noEF bicrystals. However, the interface specific ELNES signatures are less localized than the structural grain boundary expansions, consistent with previous studies of delocalization and non-local effects of the inelastic electron scattering processes.¹⁸

ELNES line shapes obtained from the grain boundary core of the EF bicrystals are different from those of the noEF bicrystals. For the EF bicrystals, the Ti L_{2,3} edges exhibit a reduction of the crystal field splitting by 0.3 ± 0.1 eV (see 1st derivative spectra in Fig S1a of the supplementary materials), indicating geometric distortions of TiO₆ octahedra within the grain boundary core.¹⁹ Interfacial L_{2,3} edges acquired from the noEF bicrystals do not resolve a crystal field splitting under identical experimental conditions (Figure 4a). Unlike the EF bicrystals, the edge onset of the interfacial Ti L_{2,3} edges recorded from the noEF bicrystals consistently reveals chemical shifts ranging between 0.3 ± 0.1 eV and 0.6 ± 0.1 eV towards lower energy losses (cf. 2nd derivative spectra in Figure S1b). These observations suggest local reduction of the Ti oxidation state, likely due to the introduction of oxygen vacancies (Figure 4b).²⁰ The O-K ELNES obtained from the grain boundary core of the EF bicrystals resembles bulk Ti₂O₃ or distorted TiO₆ octahedra (Figure 3b), which is consistent with the observed absence of a chemical shift for the Ti L_{2,3} edge.^{14,16} Thus, it is concluded that the grain boundary core of the EF bicrystals is comprised of distorted TiO₆ octahedra, while the grain boundary core of the noEF bicrystals is subject to increased oxygen vacancy concentration that leads to local reduction of titanium cations.

Characterization of the atomic and electronic structures demonstrates that application of an electrostatic field during diffusion bonding of SrTiO₃ bicrystals leads to significant structural rearrangements within grain boundary cores, including decreased local oxygen vacancy concentration. These results were reproducible over multiple bicrystals and several TEM samples prepared from each diffusion bonded grain boundary (see Figures S2 and S3 in the supplementary materials). Biasing of the half crystals before the initiation of diffusion bonding generates opposite charges on the free (100) surfaces (cf. inset in Figure 1). According to Hanzig et al. the (100) surface on the cathode side assumes oxygen stoichiometry, while the anodic (100) surface is characterized by excess oxygen vacancies.¹⁰ The resulting local oxygen concentration gradient causes the formation of the narrower grain boundary core observed in Figure 2.^{6,21} Under such conditions, generation of an asymmetric grain boundary core and space charge configuration of the EF bicrystals would be expected.²² However, on single-crystalline SrTiO₃ sufficient oxygen vacancy mobility at room temperature enables charge redistribution after the applied bias is removed.¹⁰ It is, therefore, concluded that the symmetric electronic structure, i.e., oxygen vacancy distribution, observed in Figure 3 results from appreciable vacancy mobility. Future studies of oxygen vacancy distributions and dopant segregation in the presence electric fields are required to confirm this hypothesis and quantitatively determine the proposed charge redistribution.

Dielectric properties of the bicrystals were measured over a frequency range of 10 Hz to 10 MHz to investigate how the application of an electric field affects the overall functional properties of the bicrystal samples. The dielectric response is fully capacitive at room temperature, and thus, corresponds to a combination of electrode, bulk, and grain boundary responses. To ascertain contributions from bulk SrTiO₃, the dielectric constant of (100) SrTiO₃

single crystal was determined and reproduced values from previous studies.²³ At 10^5 Hz, the dielectric constant of the EF bicrystal is 413 ± 0.3 , compared to 387 ± 12 for the noEF bicrystal (see Figure S4 in the supplementary materials for additional information). Since the EF and noEF bicrystals were bonded under otherwise identical experimental conditions, the applied electric field during diffusion bonding must have affected the observed dielectric response. Minimal distortion of the perovskite structure and low oxygen loss due to application of an electric field affects the electrical properties of SrTiO_3 . Decreases in oxygen vacancy concentration increase resistivity, thereby improving overall dielectric properties.^{3,24} A reduction of the dielectric constant in the low frequency range also corresponds to decreased oxygen vacancy concentration, which preserves stoichiometry and minimizes ferroelectric effects.²⁵ Future impedance spectroscopy experiments at higher temperature and over a wider frequency interval will enable the separation of bulk and grain boundary contributions. However, such experiments were beyond the scope of this paper.

In summary, this study demonstrates that the application of an electric field during grain boundary formation creates dissimilar atomic and electronic grain boundary configurations. Considering the success of field-assisted sintering technology, this discovery for the model system SrTiO_3 identifies the general interaction of externally applied electric fields with space charge zones surrounding internal interfaces. Electric fields applied during ceramic manufacturing are therefore expected to be capable of tailoring specific grain boundary configurations without the addition of dopant elements.

Supplemental material: Included are first and second derivative spectra of the Ti $L_{2,3}$ edges for assessment of chemical shifts and reduced crystal field splittings, as well as additional STEM micrographs and EELS data to illustrate reproducibility. The supplemental materials also include plots of experimentally determined dielectric functions.

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References

- 1 Tadao Watanabe, *Journal of Materials Science* **46** (12), 4095 (2011); Yet-Ming Chiang, W David Kingery, and Dunbar P Birnie, *Physical ceramics: principles for ceramic science and engineering*. (J. Wiley, 1997).
- 2 K. Szot, W. Speier, R. Carius, U. Zastrow, and W. Beyer, *Physical review letters* **88** (7), 075508 (2002); Markus Vollman and Rainer Waser, *Journal of the American Ceramic Society* **77** (1), 235 (1994).
- 3 I. Denk, J. Claus, and J. Maier, *Journal of Electrochemical Society* **44** (10), 3526 (1997).
- 4 Yamamoto Takahisa, Yuichi Ikuhara, and Taketo Sakuma, *Journal of Materials Science Letters* **20**, 1827 (2001); Roger A. Souza, Jurgen Fleig, and Joachim Maier, *Journal of the American Ceramic Society* **86** (6), 922 (2003); E. P. Gorzkowski, M. J. Pan, B. Bender, and C. C. M. Wu, *Journal of Electroceramics* **18** (3-4), 269 (2007).
- 5 U Anselmi-Tamburini, JE Garay, and Zuhair A Munir, *Scripta materialia* **54** (5), 823 (2006); Wei Qin, Hasti Majidi, Jondo Yun, and Klaus Benthem, *Journal of the American Ceramic Society* **99** (7), 2253 (2016).
- 6 T. Leisegang, H. Stocker, A. A. Levin, T. Weissbach, M. Zschornak, E. Gutmann, K. Rickers, S. Gemming, and D. C. Meyer, *Physical review letters* **102** (8), 087601 (2009).
- 7 Huiqing Fan and Hyoun-Ee Kim, *Journal of applied physics* **91** (1), 317 (2002).
- 8 D.C. Meyer, A.A. Levin, S. Bayer, A. Gorbunov, W. Pompe, and P. Paufler, *Applied Physics A* **80**, 515 (2005).
- 9 H. Stocker, M. Zschornak, T. Leisegang, I. Shakhverdova, S. Gemming, and D. C. Meyer, *Crystal Research and Technology* **45** (1), 13 (2010).
- 10 Juliane Hanzig, Matthias Zschornak, Florian Hanzig, Erik Mehner, Hartmut Stöcker, Barbara Abendroth, Christian Röder, Andreas Talkenberger, Gerhard Schreiber, David Rafaja, Sibylle Gemming, and Dirk C. Meyer, *Physical Review B* **88** (2) (2013).
- 11 Lauren A Hughes and Klaus van Benthem, *JoVE (Journal of Visualized Experiments)* (120), e55223 (2017).
- 12 Masaru Nishi, Tomohito Tanaka, Katsuyuki Matsunaga, Yuichi Ikuhara, and Takahisa Yamamoto, *Materials Transactions* **45** (7), 5 (2004); Teruyasu Mizoguchi, Yukio Sato, James P. Buban, Katsuyuki Matsunaga, Takahisa Yamamoto, and Yuichi Ikuhara, *Applied Physics Letters* **87** (24), 241920 (2005).
- 13 L. Fitting, S. Thiel, A. Schmehl, J. Mannhart, and D. A. Muller, *Ultramicroscopy* **106** (11-12), 1053 (2006).
- 14 G. Z. Zhu, G. Radtke, and G. A. Botton, *Nature* **490** (7420), 384 (2012).

- 16 Takahisa Yamamoto, Fumiyasu Oba, Yuichi Ikuhara, and Taketo Sakuma, *Materials*
 17 *Transactions* **43** (7), 1537 (2002).
 18 R Brydson, H Sauer, W Engel, and F Hofer, *Journal of Physics: Condensed Matter* **4**, 9 (1992).
 19 M.M. McGibbon, N.D. Browning, M.F. Chrisholm, A.J. McGibbon, S.J. Pennycook, V.
 20 Ravikumar, and V.P. Dravid, *Science* **266** (5182), 102 (1994).
 21 M. P. Oxley and L. J. Allen., *Physical Review B* **57** (6), 10 (1998).
 22 K. van Benthem, R.H. French, W. Sigle, C. Elasser, and M. Ruhle, *Ultramicroscopy* **86**, 303
 23 (86).
 24 R. D. Leapman, L. A. Grunes, and P. L. Fejes, *Physical Review B* **26** (2), 614 (1982).
 25 Ingrid Denk, Frank Noll, and Joachim Maier, *Journal of the American Ceramic Society* **80** (2),
 279 (1997).
 R. A. De Souza, *Advanced Functional Materials* **25** (40), 6326 (2015).
 RC Neville, B Hoeneisen, and CA Mead, *Journal of Applied Physics* **43** (5), 2124 (1972).
 Rainer Waser, *Journal of the American Ceramic Society* **73** (6), 1645 (1990).
 Zhi Yu, Chen Ang, and L. E. Cross, *Applied Physics Letters* **74** (20), 3044 (1999).

Figure captions:

Figure 1: Sketch of experimental set up. (100) surfaces of two SrTiO₃ single crystals are aligned with a nominal misorientation angle of 41° about their normal direction. Crystals are placed between plane-parallel Pt-Rh electrodes with Al₂O₃ slabs covered in ZrO₂ particles separating the electrodes and SrTiO₃. This stack is positioned in a MTS uniaxial tensile tester and clamshell high temperature furnace. The inset illustrates enrichment of interface plane with oxygen ions and oxygen vacancies for the SrTiO₃ single crystal acting as cathode or anode, respectively. Color gradient in the inset represents expected concentration profile.

Figure 2: HAADF-STEM images of the EF bicrystal with (a) lower half-crystal in <100> and (b) upper half-crystal in <110> zone-axis orientation; (c) and (d) show images of the noEF bicrystal in the same zone-axis orientations. Observations are consistent over extended interface lengths, several TEM samples and multiple bicrystals.

Figure 3: Background-stripped near-edge fine structures for the (a) Ti L_{2,3}- and (b) O K-edges extracted from spectrum images across the grain boundary plane of the EF bicrystal. ELNES line shapes indistinguishable from bulk SrTiO₃ are plotted in black. Interface

specific ELNES data are plotted in red. Spectra were acquired with a spatial separation of 0.4 nm and a dwell time of 1.2 s/spectrum. Each plotted spectrum is an average of 5 acquired spectra from the same area. From the Ti $L_{2,3}$ edges recorded from the grain boundary core a reduction of the crystal field splitting by 0.3 ± 0.1 eV is observed (see vertical lines to guide the eye).

Figure 4: (a) Background-stripped near-edge fine structures for the (a) Ti $L_{2,3}$ - and (b) O K-edges extracted from spectrum images across the grain boundary plane of the noEF bicrystal. ELNES line shapes indistinguishable from bulk SrTiO_3 are plotted in black. Interface specific ELNES data are plotted in blue for the noEF bicrystal. Spectra were acquired with a spatial separation of 0.4 nm and a dwell time of 1.2 s/spectrum. Each plotted spectrum is an average of 5 acquired spectra from the same area. Compared to bulk SrTiO_3 a chemical shift of -0.3 ± 0.1 eV is observed for the Ti $L_{2,3}$ edges recorded from the grain boundary core (see markings to guide the eye).







