

RESEARCH ARTICLE OPEN ACCESS

Precise Nanoscale Mapping of Electric Fields Across Random Grain Boundaries in Polycrystalline Oxides Using Precession-Assisted 4D-STEM

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Received: 16 April 2026 | **Revised:** 12 September 2026 | **Accepted:** 18 September 2026

Keywords: 4D-STEM | electron beam precession | oxide ceramics | space charge layer | STEM-DPC

ABSTRACT

Space charge layers (SCLs) at grain boundaries play a crucial role in modulating electric fields and thereby influence functional properties of materials. However, experimental analysis of these localized electric fields and the corresponding charge distribution remains challenging. Conventional center-of-mass (CoM) analysis in scanning transmission electron microscopy differential phase contrast (STEM-DPC) is strongly affected by orientation-dependent contrast and dynamical scattering. Here, we demonstrate that combining electron beam precession with advanced post-processing, employing iterative edge detection and singular value decomposition (SVD), enables reliable, unbiased diffraction shift measurements with minimal crystallographic artefacts. The new method accurately refines the central disk position in nanobeam electron diffraction (NBED) patterns and thus significantly improves the extraction of the local electric field and corresponding charge distribution. Comparison with conventional CoM methods shows superior accuracy and robustness for random grain boundaries in BaTiO₃ and SrTiO₃ as exemplary case studies. The experimental work is complemented by atomistic simulations to separate the electric field of the SCL from the mean inner potential difference of the grain boundary and the elemental segregation around the grain boundary. The in-depth analysis shows that our approach enables high-fidelity mapping of electromagnetic fields and their charge distribution in complex polycrystalline specimens for improved quantitative analysis.

1 | Introduction

The SCL around grain boundaries in non-conducting ceramics critically modulates the local electric field and thereby influences

key functional properties of materials, such as oxygen vacancy migration and ionic conductivity in oxide ceramics [1–8]. Quantitative mapping of the local electromagnetic field is essential not only for understanding fundamental mechanisms, but also for

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advancing applications in electronic devices, magnetic storage media, and quantum materials [3, 9–11]. Various techniques have been explored for high-resolution field mapping, including off-axis electron holography and scanning transmission electron microscopy based differential phase contrast (STEM-DPC) imaging [12–20]. Off-axis electron holography can directly record the phase shift of the electron wave to visualize electrostatic potentials and magnetic induction, but it requires a specialized transmission electron microscope (TEM) with a biprism and a coherent reference wave within the field of view [12–14], and in practice suffers from phase-wrapping artifacts and strict noise/dose constraints. As a complementary approach, STEM-DPC measures the beam deflection by determining either the rigid shift of the diffraction pattern or the redistribution of intensity within the direct beam, offering real-space field maps without the need for a coherent reference wave [21–25]. However, traditional STEM-DPC implementations using a segmented detector have limited sensitivity and are prone to background drifts. Even more critical, diffraction contrast from crystallographic features imposes significant systematic, orientation-dependent shifts, making it challenging to identify the true electric field signal [26]. These challenges become particularly pronounced in heterogeneous specimens, where asymmetric or randomly oriented grain boundaries, local thickness variations, and crystallographic misorientations lead to inhomogeneous bright-field disk intensities that distort the true DPC signal.

Four-dimensional scanning transmission electron microscopy (4D-STEM) equipped with high-angular-resolution pixelated detectors has enabled improved data acquisition and processing for visualizing internal electric fields in materials [15, 26–28]. By recording a full diffraction pattern at every probe position, 4D-STEM can capture subtle beam deflection caused by local electric and magnetic fields [29–31]. However, reliably extracting the electric field components from 4D-STEM data remains challenging, as diffraction contrast variations arising from orientation, thickness, and multiple scattering often obscure the field-induced shifts. To address these limitations, Nakamura et al. proposed a tilt-series DPC method, where multiple STEM-DPC images are acquired at slightly varied specimen tilts [32]. By averaging these images, orientation-sensitive diffraction contrast can be reduced while reinforcing the tilt-insensitive electromagnetic field signals. This approach has been successfully applied to semiconductor p–n junctions and ceramic bicrystals using momentum-resolved 4D-STEM without beam precession [15, 30, 33]. Alternatively, electron precession can be employed to reduce diffraction contrast and multiple scattering [18, 24, 34]. However, even high precession angles of $\sim 1^\circ$ are not sufficient to fully eliminate diffraction contrast in polycrystalline ceramics, which typically exhibit broad orientation distributions and complex grain boundary networks. In this case, CoM fitting, widely used to track disk shifts in 4D-STEM, can suffer from serious artefacts in polycrystalline materials due to remaining asymmetric intensity distributions within the central diffraction disk, caused by local misorientations and dynamic scattering [34]. To overcome this, recent studies introduced a 4D-STEM approach that uses edge detection algorithms to extract the disk boundary more reliably from diffraction patterns [28, 31, 34–37]. While these methods reduce intensity redistribution effects caused by the local crystal orientation and thickness and thus allow more precise and robust disk tracking, they were only demonstrated

for systems with strong DPC signals, such as semiconducting junctions, micrometer-scale Landau domains, or vortex structures in magnetic materials. To date, a systematic investigation of the precision and reliability of DPC measurements, artifact suppression, and thus the ability to reliably measure small diffraction displacements in polycrystalline materials has not been reported. Especially for the subtle nanometer scale electric field variations in SCLs around random grain boundaries, precise measurement and artifact suppression are critical.

In this study, we extend electromagnetic field mapping to complex polycrystalline oxides targeting weak SCL-related electric fields at random grain boundaries. For this purpose, we combine electron beam precession with a robust post-processing workflow based on Sobel filter edge detection of the bright-field disk and SVD-based disk-center refinement. In randomly oriented polycrystalline specimens, the true field-induced disk shift is small and can be easily obscured by orientation-dependent diffraction contrast, dynamic scattering, and local thickness variations. The workflow presented here addresses these challenges by reducing diffraction contrast contributions during acquisition and by determining the disk shift from the geometrical edge of the bright-field disk during post-processing. We validate this approach by comparison with simulated grain boundaries and the associated local field distribution and by direct comparison of conventional CoM and SVD analysis with and without precession, demonstrating that the combined precession-SVD workflow results in the lowest residual background variation and highest data reliability. This enables large-area electric-field mapping across randomly oriented grains and provides access to weak DPC signals that are difficult to extract using conventional CoM-based analysis. The refined field measurements are further used to derive electrostatic potential and charge-density distributions, allowing the local electrostatic response to be correlated with grain boundary structure and dopant segregation in barium titanate (BTO) and strontium titanate (STO). Complementary atomistic simulations show that the measured response is dominated by the SCL contribution, but segregation-induced mean-inner-potential variations near the grain boundary core must be considered for a quantitative interpretation.

2 | Methods

2.1 | Sample Preparation

Fe-doped BaTiO₃ (BTO) bulk ceramics were prepared by conventional solid-state reaction using stoichiometric mixtures of BaCO₃ and TiO₂ with Fe₂O₃ as the Fe precursor. The nominal Fe content was 2.4 at% on the Ti site. The precursor powders were ball milled in ethanol for 24 h. After drying, the powder mixture was calcined in air at 1250°C for 2 h. The calcined powder was uniaxially pressed into pellets (10 mm in diameter and approximately 1.5 mm in thickness) at 200 MPa and sintered in air at 1450°C for 4 h. Fe-doped SrTiO₃ (STO) bulk ceramics were prepared by conventional solid-state reaction using stoichiometric mixtures of SrCO₃ and TiO₂ with Fe₂O₃ as the Fe precursor. The nominal Fe content was 2 at% on the Ti site. The precursor powders were ball milled in isopropanol with 3 mm ZrO₂ balls using a PM400 planetary ball mill for 15 cycles of 5 min at 400 rpm. The powders were sieved and calcined at 975°C for 3 h, followed by a second milling step

of 6 cycles of 5 min at 300 rpm. Green bodies were uniaxially prepressed, cold-isostatically pressed at 400 MPa, and sintered in air at 1350°C for 1 h. The furnace heating and cooling rates were 20 and 10 K min⁻¹.

Thin lamellae for TEM analysis were prepared from the bulk oxides by focused ion beam (FIB) milling using a Strata 400 S (FEI). Final thinning was performed to achieve a thickness of approximately 50–100 nm for electron transparency at the area of interest, employing a stepwise reduction in accelerating voltage from 30 to 5 kV and beam currents from 8 nA to 2 pA to minimize Ga⁺ ion-induced damage. Selected lamellae were further polished using a NanoMill (Fischione) to 500 eV.

Large-area STO samples were prepared by conventional TEM specimen preparation. The sintered ceramics were cut and dimpled, followed by ion polishing using a PIPS II ion mill (Gatan) with a final milling energy of 200 eV.

2.2 | Atomic Structure Simulations

Atomic configurations of a BaTiO₃ Σ5 tilt boundary were constructed using molecular dynamics (MD) simulations implemented in the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) package. The initial model consisted of a bicrystal supercell with a Σ5(310)[001] symmetric tilt boundary placed at the center of a 25 nm cubic simulation box. The bicrystal was generated by joining two single-crystal BTO slabs with a relative rigid-body translation to identify the lowest-energy grain boundary configuration. Interatomic interactions were described using an atomic cluster expansion (ACE) machine learning potential [38] parameterized for BaTiO₃ using the PACE-MAKER code [39] to accurately reproduce the lattice dynamics, ferroelectric properties, and defect energetics of the material. After initial construction, the system was relaxed using energy minimization and subsequently equilibrated under the constant particle number, pressure and temperature (NPT) ensemble at 700 K and 0 bar using the Nosé–Hoover thermostat and barostat to ensure thermal and mechanical stability of the structure. To obtain a well-relaxed grain boundary configuration, multiple grain boundary translations along the boundary plane were tested, and the configuration with the lowest potential energy was selected. Structural relaxation was followed by additional short MD runs at room temperature to allow for local reconstruction and to minimize residual stresses near the boundary. The final atomic structure was analyzed to investigate coordination changes and defect energies near the grain boundary.

2.3 | Experiment-Driven Atomistic Model Modification, Mean Inner Potential and Space Charge Layer

The atomic structure described above was used as the initial atomic model. The simulation cell (785.20955 × 12.62398 × 3.99205 Å³) was replicated to implement compositional modification resulting in a supercell of 785.20955 × 782.68697 × 99.80135 Å³. Two atomic models were constructed for subsequent simulations, an undoped reference model and an Fe-doped model. To construct the Fe-doped model, Fe segregation and oxygen defect

concentrations were introduced to resemble the experimental STEM energy dispersive X-ray spectroscopy (EDS) composition in the SCL (Figure S1), with the observed segregation width of 10 nm to define a Gaussian spatial weighting function. Fe segregation was implemented by substituting Fe atoms for Ti according to this weighting function, reproducing the measured Fe/Ti ratio of 0.064 next to the grain boundary and 0.021 in the bulk. The oxygen deficiency at the grain boundary is present from the MD model. Additional oxygen deficiency in the bulk was introduced by probabilistic removal of O atoms, with a higher removal probability in the bulk than in the SCL, to mimic the oxygen-vacancy depletion expected in a conventional positive-core space-charge layer. The target oxygen distribution was guided by the defect-chemistry-informed phase-field model of Wang et al. [40].

The mean inner potential for the two structures has been calculated in abTEM [41] using an independent atom model. The mean inner potential (MIP) calculation based on the independent atom model should be regarded as a semi-quantitative reference (Figure S2). The model does not fully include dopant valence variations, charge transfer, or the exact atomic structure of the experimentally measured random grain boundary, but provides a reasonable unit cell level estimate of MIP changes across the grain boundary. The projected potential has been convoluted with a Gaussian profile with a diameter of the lattice parameters to reflect the experimental electron beam diameter and further averaged along the grain boundary to calculate the mean inner potential profiles across the boundary. Analogously, line profiles of the atomic fractions of the different elements have been calculated by projecting the atomic counts along the grain boundary, convolving them with a Gaussian profile, and normalizing them to the bulk atomic density.

The space-charge potential used in the present analysis was adopted from the continuum restricted-equilibrium model reported by Usler et al. [42] for acceptor-doped SrTiO₃. In that work, the space-charge potential was obtained as the grain-boundary-to-bulk potential difference by solving the Poisson equation self-consistently with defect-chemical relations and site-exclusion constraints, while accounting for oxygen-vacancy segregation at the grain-boundary core and frozen-in acceptor and oxygen-vacancy distributions under restricted-equilibrium conditions.

2.4 | STEM and 4D-STEM Experiment

Conventional STEM measurements were performed using a probe-corrected Themis 300 (Thermo Fisher Scientific, TFS) at an operation voltage of 300 kV in microprobe STEM mode. Spot size 5 and a semi-convergence angle of 2.5 mrad were employed, resulting in a diffraction-limited probe size of approximately 0.5 nm. High-angle annular dark-field (HAADF) images were acquired in this mode with a camera length of 380 mm and a collection angle of 21–125 mrad.

EDS measurements were conducted using a Super-X G2 detector system integrated within the Themis 300 microscope. The same beam settings were employed for HAADF imaging. Spectral data were acquired with a dwell time of 40 μs per pixel. The detector

was operated with a dispersion of 5 eV, an energy offset of −250 eV, and a shaping time of 3 μ s. All four segments of the Super-X detector were active during acquisition, ensuring high solid angle coverage.

For the 4D-STEM measurements, different experimental conditions were applied depending on the measurement purpose. For electric field measurement, a convergence angle of 2.5 mrad was employed to prevent overlap between the diffraction disks and the direct beam, ensuring clear separation for reliable analysis. Diffraction patterns were recorded using a Quadro detector (DECTRIS) at a camera length of 3.1 m to magnify the direct beam and enhance DPC sensitivity. The acquisition time was set to 1 ms per probe position, with a scan step size of 5 Å for higher resolution imaging focused on the grain boundary and 5 nm for lower resolution large field of view mapping. One 4D-STEM data set was acquired without precession and a second corresponding one with precession applied using a Nanomegas system with a precession angle of 0.6°, performed with a single rotation per probe position. The orientation map was processed using the commercial ASTAR software (Nanomegas). For measuring the strain field, a smaller convergence angle of 0.5 mrad and a camera length of 460 mm were employed to achieve higher angular resolution in the diffraction patterns. A step size of 5 Å across the grain boundary was used in this configuration.

The local specimen thickness in the analyzed regions was estimated from the 4D-STEM diffraction patterns using the integrated intensity of the bright-field disk. The integrated bright-field (BF) disk intensity was first measured from a vacuum diffraction pattern, I_0 , acquired under the same optical and detector conditions. The corresponding integrated BF-disk intensity from the sample region, I , was then measured, and the relative thickness estimated using the logarithmic intensity attenuation, $\frac{I}{I_0} = \ln\left(\frac{I_0}{I}\right)$, where λ_{eff} is the effective elastic mean free path under the present experimental conditions. For the present 300 kV measurements, λ_{eff} was estimated to be approximately 140 nm for BTO and 145 nm for STO, following the density-based empirical mean-free-path formulation of Iakoubovskii et al. [43] To reduce the influence of local crystallographic orientation and diffraction contrast, the BF-disk intensity was averaged over multiple sample positions across the analyzed region before performing the log-ratio calculation. This analysis gave an estimated local thickness of 80 ± 20 nm for the BTO region and 60 ± 30 nm for the STO region. These values were used for converting the projected DPC deflection into the local electric field.

2.5 | Data Processing for Bright-Field Disk Shift and Electric-Field Mapping

To retrieve the projected electric field from the 4D-STEM datasets, we determined the displacement of the central bright-field disk using a geometry-based edge-fitting method. This approach enables precise determination of beam deflection by estimating the displacement of the disk with sub-pixel precision.

Each diffraction pattern was preprocessed by applying a two-dimensional Hanning window, which was logarithmically scaled and normalized to enhance the visibility of the central disk while

suppressing background and boundary artifacts. An optimized Sobel edge detection filter was applied to identify the boundary of the bright-field disk. A pattern-specific adaptive thresholding algorithm was employed, where the threshold value was dynamically optimized for each diffraction pattern to yield a clean and continuous edge contour without including spurious features. Unlike methods that rely on the intensity distribution or diffraction ring shape, this edge-based method directly captures the geometric boundary of the central disk [31, 35]. This strategy reduces the influence of diffraction contrast and crystal orientation effects, allowing for more precise measurement of rigid beam shifts. This is particularly advantageous in regions where intensity asymmetries or diffraction contrast can bias CoM-based measurements. The edge-fitted disk shift can be interpreted quantitatively as an electric-field-induced beam deflection when the mean inner potential does not vary significantly within the STEM probe, leading to an approximately uniform displacement of the central bright-field disk. This condition is well satisfied outside the structurally abrupt grain boundary core, especially in the extended SCL region, where the electric field varies over a length scale significantly larger than the probe diameter. In this region, the disk edge remains well defined, and the fitted disk shift represents the electric field averaged over the local scattering volume. At the grain boundary core itself, however, the interpretation is more complex because the atomic structure, mean inner potential, local elemental distribution, defect configuration, and possible channeling conditions may change within the probe diameter and along the beam path. Under these conditions, the diffraction disk is not rigidly shifted, as already discussed in previous momentum-resolved DPC studies [19, 34, 36]. Therefore, the narrow grain boundary core is excluded from quantitative electric-field interpretation and is treated only as a non-quantitative core response, whereas reliable quantitative electric-field analysis is possible in the extended SCL region. The detected edge coordinates were fitted to an ellipse using an algebraic conic fitting algorithm based on SVD. The ellipse was modeled using the general second-order form:

$$\mathbf{F}(\mathbf{C}, \mathbf{Q}) = \mathbf{C} \cdot \mathbf{Q} = aq_x^2 + bq_xq_y + cq_y^2 + dq_x + eq_y + f$$

where $\mathbf{C} = [a \ b \ c \ d \ e \ f]$ and $\mathbf{Q} = [q_x^2 \ q_xq_y \ q_y^2 \ q_x \ q_y \ 1]^T$. $\mathbf{F}(\mathbf{C}, \mathbf{Q})$ is the mismatch distance of a data point (q_x, q_y) to the ellipse $\mathbf{F}(\mathbf{C}, \mathbf{Q}) = 0$. Thus, the best fit of an ellipse to the edge of the diffraction disk is equivalent to finding $\mathbf{C}$ to minimize the sum of squared mismatch distances $\mathbf{D}(\mathbf{C}) = \min \sum_{i=1}^N \mathbf{F}(\mathbf{C}_i, \mathbf{Q}_i)^2$, where N is the total number of selected pixels by the thresholding, and i is the pixel sequence number. This least square problem can be solved by SVD considering a rank-deficient generalized eigenvalue system, as $\mathbf{Q}\mathbf{Q}^T \mathbf{C}^T = \lambda \mathbf{P}\mathbf{C}^T$, where $\mathbf{P}$ is a constraint matrix to avoid trivial solutions, e.g., $\mathbf{C} = 0$, as defined by

$$\mathbf{P} = \begin{bmatrix} 0 & 0 & -2 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ -2 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix}$$

The fitted parameters were converted into the center position and radius. The displacement of the fitted ellipse center relative to a reference position was used to calculate the transverse

momentum transfer, $\Delta p_{\perp}$, and the corresponding in-plane electric field according to $E_{\perp} = \frac{v\Delta p_{\perp}}{e\Delta z}$, where v is the electron velocity, e is the elementary charge, and Δz is the local specimen thickness estimated as described in Section 2.4. A vacuum reference acquired under the same optical conditions was used to correct the systematic beam-shift offset.

The electrostatic potential across the grain boundary was obtained from the corrected electric-field component normal to the boundary using $V(x) = \int E_{\perp}(x)dx$. The integration was performed numerically using the cumulative trapezoidal method, with the initial point defined as zero potential. The corresponding charge density was calculated from the spatial gradient of the electric field using Gauss's law, $\rho(x) = \epsilon_0 \epsilon_r dE_{\perp}(x)/dx$, and converted to units of C/nm^3 . Here, $\epsilon_r = 1$ was used, such that the resulting quantity represents the effective charge density associated with the measured field gradient. For the two-dimensional electrostatic potential map, the potential was reconstructed numerically from the in-plane electric-field components using partial integration. The corresponding charge-density map was obtained from the spatial partial derivatives of the electric-field components using Gauss's law.

The quantitative interpretation of the reconstructed electrostatic profiles is subject to several experimental limitations. Residual offsets in the measured electric field can accumulate during numerical integration and affect the reconstructed potential. This contribution is minimized by vacuum-reference correction and by defining the potential relative to the initial point of the integration profile. In addition, the measured electric field is probe-convolved and averaged through the local specimen thickness Δz . Uncertainty in Δz therefore mainly affects the absolute field magnitude, while the finite probe size broadens highly localized field variations near the grain-boundary core. However, the approximately 0.5 nm probe is substantially smaller than the characteristic width of the extended SCL and averages over a larger local region than highly convergent atomic-resolution probes, reducing sensitivity to atomic-scale field variations while retaining the smoother electric-field response of the extended SCL. Quantitative interpretation of the grain-boundary core remains limited because local structural and mean inner potential variations occur on a length scale comparable to the probe size. Possible specimen, surface, or beam-induced charging cannot be independently separated from the measured signal and therefore remains an additional source of uncertainty. Consequently, the quantitative analysis is focused on the extended SCL region, whereas the absolute magnitude and highly localized response at the grain-boundary core are interpreted with caution.

2.6 | Cepstral Analysis for Strain Mapping

Strain mapping was carried out using cepstral analysis applied to each diffraction pattern in the 4D-STEM dataset [44]. This method utilizes the Fourier transform of diffraction features in reciprocal space to extract local lattice parameter variations with high spatial resolution. Specifically, the logarithm of the Fourier transform of each diffraction pattern was computed to obtain the cepstrum, which emphasizes periodic modulations corresponding to the underlying lattice spacings. A band-pass filter was applied in the cepstral domain to isolate the frequency

components associated with the Bragg disk spacing. The resulting filtered signal was then analyzed to extract the positions of the cepstral peaks, which reflect the periodicity and orientation of the diffraction pattern. By measuring shifts and distortions in these cepstral features across the scan, local strain components were derived. Compared to direct-space geometric methods, e.g., template matching or Hough transformation, cepstral strain mapping provides enhanced robustness against variations in intensity, crystal orientation, and probe aberrations. Since the analysis is based on the periodicity of reciprocal lattice information rather than the absolute position or shape of individual Bragg disks, it is less sensitive to local orientation variation and diffraction contrast. Moreover, it significantly reduces errors associated with excitation conditions, as it does not rely on satisfying the exact Bragg condition at each scan point. This allows for more robust and stable strain quantification even in regions with strong orientation gradients, grain boundaries, or slight misalignments. The analysis was performed using the MATLAB-based software package developed by Padgett et al. [44], which implements the full cepstral workflow including Fourier transformation, filtering, peak detection, and strain tensor reconstruction.

To further correlate the local strain state with variations in the mean inner potential (MIP), we computed the volumetric strain ϵ_{Vol} from the reciprocal lattice vector deformation, assuming the third dimension to be uniform. As illustrated in Figure 1e, two non-collinear reciprocal lattice vectors g_1 and g_2 were selected from each diffraction pattern, and their local strain components were calculated as $\epsilon_{g1} = \frac{|g_1 - g_{1,0}|}{g_{1,0}}$ and $\epsilon_{g2} = \frac{|g_2 - g_{2,0}|}{g_{2,0}}$, where $g_{1,0}$ and $g_{2,0}$ represent the corresponding vectors in an unstrained reference region. The volumetric strain was then defined as $\epsilon_{Vol} = \frac{\epsilon_{g1} + \epsilon_{g2}}{2}$. This scalar measure reflects the projected change in unit cell area, which is directly related to local atomic density variations, within the bulk and the extended SCL, whereas it cannot be directly interpreted in the grain boundary core due to the strong structural variation within the core. As the mean inner potential is sensitive to electron density, the small variations observed in the volumetric strain map within the bulk and the extended SCL indicate that density-related contributions to the measured DPC signal are not significant in the SCL analysis.

3 | Results and Discussion

Figure 1 outlines the complete workflow used to map the electric field and strain distribution across a random grain boundary in polycrystalline oxides with high spatial resolution. To suppress strong diffraction contrast and enhance the sensitivity to weak electrostatic signals, we used a precession-assisted 4D-STEM technique (Figure S3). In this approach, the incident electron beam is slightly tilted around a defined cone angle during scanning (Figure 1a), allowing for an angular integration of diffraction patterns that averages out most orientation-related contrast while preserving deflection signals arising from the electric field. The central bright-field (BF) disk in each diffraction pattern was first preprocessed using a 2D Hanning window, followed by logarithmic scaling and normalization to enhance the central disk and suppress background artifacts. An optimized Sobel edge filter with adaptive thresholding was then applied to extract clean and continuous disk boundaries (Video S1). This edge-based

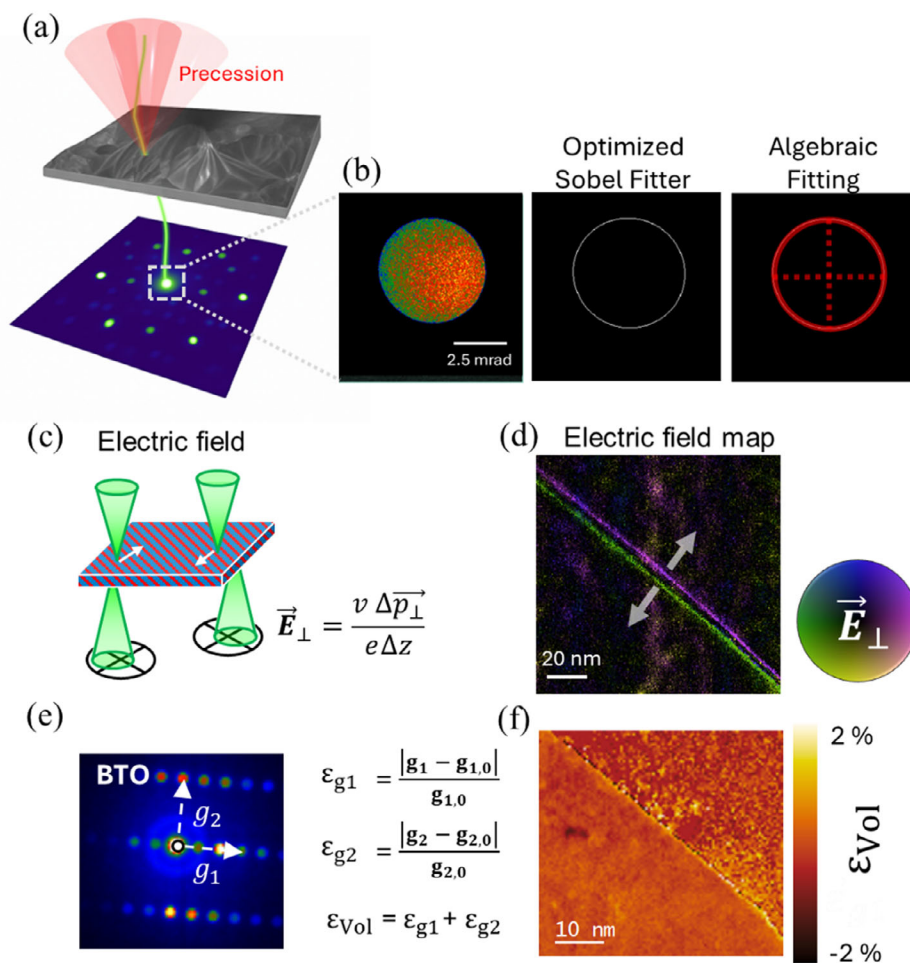


FIGURE 1 | Workflow for reliable mapping of electric field and strain across grain boundaries in polycrystalline oxides using precession-assisted 4D-STEM and SVD-based diffraction shift detection. (a) Schematic illustration of electron beam precession during 4D-STEM acquisition to reduce diffraction and orientation contrast. (b) Central bright-field disk from a diffraction pattern processed via an optimized Sobel edge filter followed by algebraic ellipse fitting using SVD to robustly extract the disk position. (c) Electric field-induced deflection of the central disk due to transverse momentum transfer, used to reconstruct the projected electric field. (d) In-plane electric field map showing sharp contrast across a grain boundary; color hue and intensity encode field orientation and magnitude in V/nm. (e) Definition of reciprocal space strain components from two non-collinear diffraction vectors used to compute volumetric strain. (f) Volumetric strain map across the boundary, used as a structural reference for assessing possible density-related contributions to the DPC signal.

method, which avoids reliance on intensity profiles or diffraction ring shapes, improves robustness against diffraction contrast and orientation effects. The resulting contour was subsequently fitted with an ellipse using SVD, as shown in Figure 1b.

By analyzing the spatial variation of the disk shift across the scanned area, we reconstructed the projected in-plane electric field map (Figure 1d). The map clearly reveals enhanced electric field contrast at the grain boundary, indicating local variations in electrostatic potential likely associated with the SCL at the boundary. To assess whether strain- or density-related MIP variations could contribute to the measured DPC signal, we simultaneously extracted local volumetric strain from reciprocal space distortion using two independent diffraction vectors (Figure 1e). The resulting volumetric strain map (Figure 1f) was used as a structural reference.

Figure 2 compares DPC maps obtained under different 4D-STEM acquisition and processing conditions in a polycrystalline region.

Figure 2a shows the BF-STEM image of the area selected for 4D-STEM acquisition, and Figure 2b shows the corresponding crystal orientation map reconstructed from the 4D-STEM dataset. Except for local variations around the grain boundaries, which are not visible due to the large scan steps used for the overview map, the sample is expected to exhibit a uniform electric field, meaning no field changes should be present. Figure 2c,d presents the DPC maps obtained using the conventional CoM method without and with beam precession. In these maps, hue represents the in-plane direction of the DPC vector and intensity represents its magnitude. The magnitude map is presented in Figure S4.

The CoM map acquired without beam precession exhibits strong spatial contrast associated with diffraction contrast due to local orientation variations, indicating that the measured DPC signal is strongly influenced by an asymmetric intensity redistribution within the BF disk due to diffraction condition variations. When beam precession is applied, the overall background variation is reduced, and some of the orientation-dependent contrast is

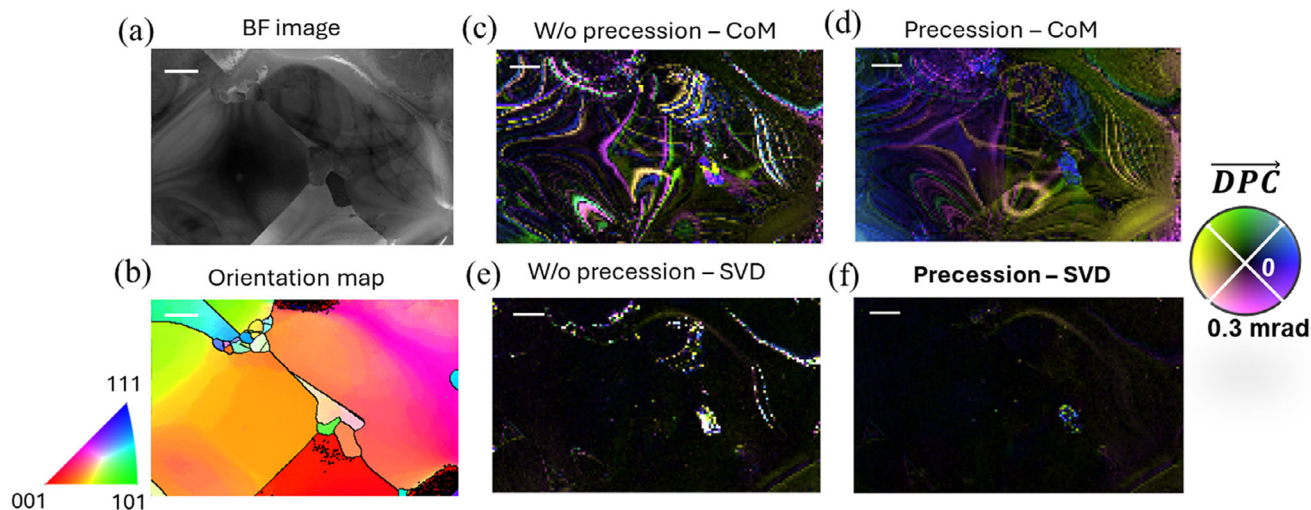


FIGURE 2 | Comparison of beam-deflection maps obtained using different 4D-STEM processing methods. (a) BF-STEM image showing the region selected for 4D-STEM acquisition, which is expected to yield a uniform field distribution. (b) 4D-STEM automatic crystal orientation map (ACOM) of the same region, showing the local crystallographic orientation distribution. (c,d) Color maps of the DPC signal obtained using the CoM method: (c) without beam precession and (d) with beam precession. (e,f) Color maps of the DPC signal obtained using the SVD-based disk center fitting method: (e) without beam precession and (f) with beam precession. In the DPC maps, hue represents the in-plane direction of the DPC vector and intensity represents its magnitude. All scale bars correspond to 1000 nm.

suppressed, showing that angular averaging during acquisition is effective in mitigating part of the diffraction contribution. Nevertheless, the CoM result with precession still exhibits substantial non-uniform contrast, demonstrating that beam precession alone is insufficient to fully remove diffraction-induced artifacts in a polycrystalline specimen. This trend is also reflected quantitatively in the standard deviation measured over the mapped region, which decreases from 0.115 mrad without precession to 0.0166 mrad with precession (histogram in Figure S5). Although this reduction is substantial, the CoM-based result with precession still exhibits a relatively high level of variation, indicating that significant diffraction-induced artifacts remain and limit interpretation of the DPC measurements in terms of the local electric field.

Figure 2e,f show the DPC maps reconstructed from the same raw data used to generate Figure 2c,d using the SVD-based disk fitting method. In contrast to the CoM results, the SVD-based maps are considerably more uniform and show markedly reduced diffraction-related contrast. This improvement is consistent with the geometry-based edge-fitting strategy used for disk shift determination, which is less sensitive to crystal-orientation-dependent intensity redistribution inside the central BF disk than the conventional CoM approach. Even without beam precession, the SVD-based reconstruction substantially lowers the variation of the measured DPC signal, giving a standard deviation of 0.0107 mrad, which is significantly smaller than that of the CoM result under the same condition. When beam precession is combined with SVD fitting, the standard deviation is further reduced to 0.0036 mrad, yielding the most homogeneous background among all cases (histogram in Figure S5). The beam-precessed SVD map in Figure 2f therefore provides the clearest representation of the intrinsic DPC contrast, with minimal artifacts from diffraction-induced background modulation. These results demonstrate that beam precession and SVD-based disk fitting act synergistically: precession suppresses orientation-

sensitive diffraction contrast during acquisition, while SVD fitting improves the robustness of disk shift retrieval during post-processing.

Figure 3 shows the DPC analysis across a random grain boundary using 4D-STEM. Figure 3a presents the angular dark-field (ADF) STEM image of the analyzed region, in which the grain boundary is clearly resolved as a diagonal interface separating two adjacent grains. The local diffraction patterns taken from the two sides of the grains are shown in Figure 3b,c. These patterns confirm a random crystallographic misorientation between the neighboring grains.

Figure 3d,e shows the DPC signal component perpendicular to the grain boundary, reconstructed using the CoM method without and with beam precession. The CoM result without precession exhibits strong spatial variations over both grains, indicating that the measured DPC signal is strongly affected by diffraction-induced intensity asymmetry within the bright-field disk. With beam precession, the broad orientation-dependent contrast is suppressed. However, noticeable background modulation remains throughout the field of view, showing that precession alone is not sufficient to fully remove diffraction-induced contributions from the CoM-based reconstruction as discussed before for polycrystalline samples.

Figure 3f,g shows the DPC maps of the signal component perpendicular to the grain boundary obtained using the SVD-based disk fitting method without and with beam precession. Compared with the CoM-based results, the SVD-based maps are substantially more uniform within the grains and show much clearer localization of the DPC contrast at the grain boundary and greater uniformity along the boundary. The improvement is most evident in Figure 3g, where the grain boundary is resolved as a narrow high-contrast feature on a fairly homogeneous background. Quantitatively, the beam-precessed SVD result exhibits a

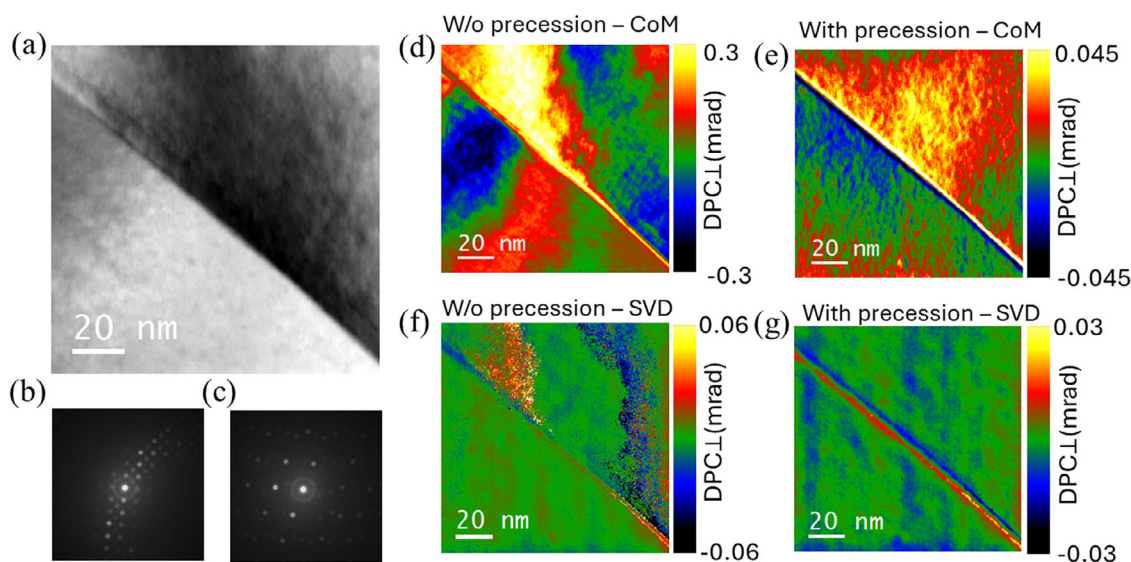


FIGURE 3 | Quantitative 4D-STEM analysis of a random grain boundary. (a) ADF-STEM image of the analyzed area containing a grain boundary. (b,c) Representative local diffraction patterns acquired from the two grains on either side of the boundary. (d,e) DPC signal perpendicular to the grain boundary obtained using the CoM method: (d) without beam precession and (e) with beam precession. (f,g) DPC signal perpendicular to the grain boundary obtained by the SVD-based disk fitting method: (f) without beam precession and (g) with beam precession.

standard deviation approximately one order of magnitude lower than that of the corresponding CoM result, confirming the strong suppression of diffraction-induced background variations. Weak residual contrast remains visible even after beam precession and SVD-based fitting. Its origin cannot be uniquely identified from the present dataset and may include local thickness or surface variations, specimen bending, or subsurface structural features. Beam-induced charging and preparation-related effects also cannot be fully excluded. However, these residual features are much weaker than the artifacts observed in the CoM-based reconstructions and do not significantly limit the identification and interpretation of the localized grain boundary DPC signal.

Figure 4 demonstrates that the present 4D-STEM approach enables correlative analysis of structural and electrostatic quantities across a single grain boundary from the same region. Figure 4a shows the ADF-STEM image of the analyzed region. Figure 4b shows the corresponding 4D-STEM ACOM crystal orientation map, confirming that the interface separates two distinct grains; the overlaid cuboids schematically indicate their crystallographic orientation. Figure 4c shows the volumetric strain map of the same area, providing structural information that can be compared directly with the electrostatic response within the same region. Figure 4d shows the in-plane electric-field map of the component normal to the grain boundary, obtained from the precessed-SVD DPC analysis. A pronounced field contrast is observed across the interface, indicating a localized electrostatic response associated with the grain boundary. Because the aim of this study was to analyze random grain boundaries in a polycrystalline specimen, the adjacent grains were not aligned to major zone axes during DPC acquisition. This geometry reduces strong channeling and dynamical diffraction effects. Instead, the specimen was tilted to make the projected grain boundary as sharp as possible, thereby minimizing projection broadening of the grain boundary / SCL signal. The projected grain boundary width estimated from the line profile in Figure 4g

is approximately 1 nm. This value is consistent with the grain boundary width estimated from the formation-energy profile in our MD simulations, supporting the conclusion that the analyzed boundary was close to an edge-on condition. Nevertheless, the reconstructed electric field and charge density represent projected and thickness averaged quantities along the electron beam direction.

Figure 4e,f shows the electrostatic potential and effective charge-density distributions derived from the measured electric field. The line profiles in Figure 4g summarize the correlated electrostatic behavior across the grain boundary. The electric-field profile shows a strong divergence on the two sides of the boundary, consistent with the presence of an interfacial electrostatic field associated with a space-charge region. At the grain boundary core, however, the situation is more complex. The atomic structure, mean inner potential, local elemental distribution, defect configuration, and possible channeling conditions can change within the probe diameter and along the beam path. Under these conditions, the diffraction disk may no longer behave as a purely rigidly shifted object. The experimentally reconstructed potential should therefore be interpreted as the more complicated projected potential response. It contains both the broader SCL-induced electrostatic potential and local MIP-related contributions at the grain boundary core. A lower atomic density at the grain boundary core is expected to reduce the local MIP, but this contribution is narrow and localized at the structurally disordered core. The reconstructed positive potential barrier away from the core is, therefore, dominated by the SCL contribution, while the grain boundary core itself has a locally reduced MIP. The charge-density profile shows positive peaks at the grain boundary core, while negative charge accumulation is observed adjacent to the core, consistent with charge compensation in the surrounding space-charge region. The sharp downward peak at the grain-boundary core should be interpreted with caution, because it includes contributions from local MIP variations associated with

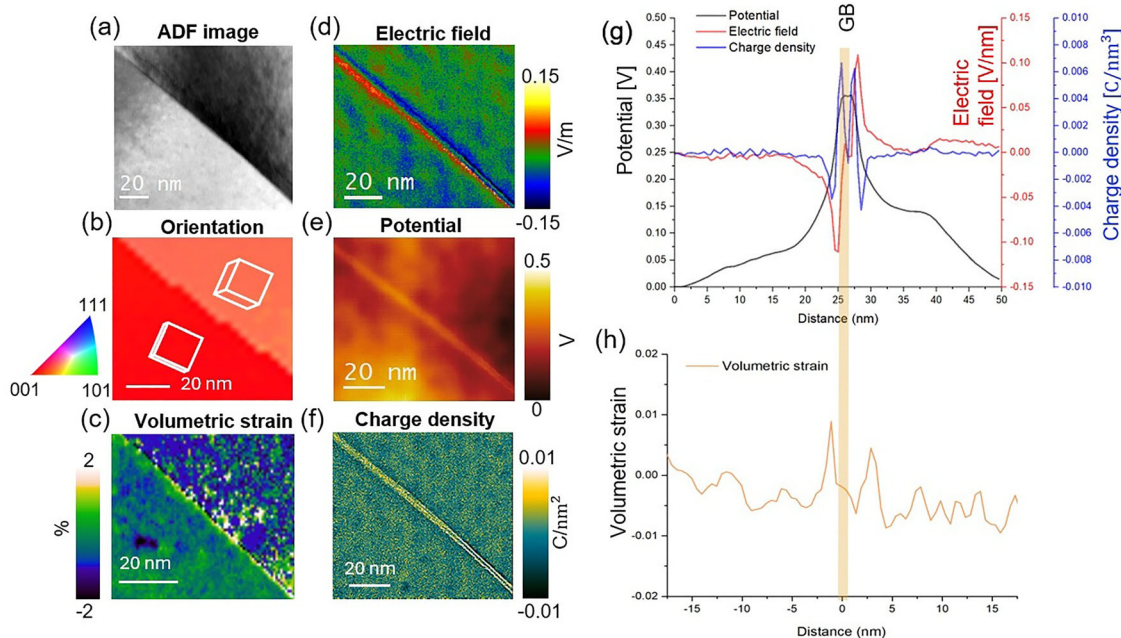


FIGURE 4 | Quantitative electrostatic potential, electric-field and charge-density analysis across a single random grain boundary using precession-assisted 4D-STEM. (a) ADF-STEM image of the analyzed region. (b) 4D-STEM ACOM orientation map indicating the two neighboring grains; the overlaid cuboids schematically represent their crystallographic orientations. (c) Volumetric strain map of the same area. (d) In-plane electric-field map showing the component normal to the grain boundary obtained by DPC analysis. (e) Electrostatic potential map derived by numerical integration of the corrected electric-field component. (f) Charge-density map calculated from the spatial gradient of the corrected electric-field component. (g) Line profiles of electrostatic potential (black), electric field (red), and charge density (blue) across the grain boundary, with the shaded band marking the grain-boundary position. (h) Volumetric strain profile across the same line. Quantitative color bars with numerical ranges and units are shown for panels (d–f). The zero level of the electric-field map corresponds to the vacuum-corrected DPC signal, and the electrostatic potential is referenced to the initial point of the integration profile.

the structurally disordered core, finite probe convolution, and the reduced validity of a purely rigid disk-shift interpretation at the core.

However, the absolute magnitudes of the reconstructed electric field, potential, and charge density may still be influenced by additional contributions, including local MIP variations at the grain boundary core, segregation-induced MIP changes near the boundary, surface charging of the cross-sectional TEM specimen, and possible effects from the FIB-damaged surface layer. These factors need to be considered when making a fully quantitative interpretation of the reconstructed electrostatic profiles.

Figure 5 provides an atomistic-model-based framework for interpreting the DPC signal across a $\Sigma 5$ grain boundary in BaTiO_3 as an exemplary case study using the experimentally measured compositional profiles for the Fe distribution. Figure 5a–c shows the grain-boundary model and the corresponding undoped and Fe-doped atomic structures, while Figure 5d,e shows the associated elemental profiles. Based on these profiles, the MIP contribution and the space-charge potential were evaluated separately and then combined, as summarized in Figure 5f. The results show that segregation-induced MIP changes can contribute to the measured DPC signal and therefore must be considered for a quantitative interpretation of the electric field in the SCL. In the present case, the space-charge contribution is noticeably larger than the MIP contribution within the SCL, with a potential variation of about 0.7 V compared with about 0.2 V from

the MIP term, indicating that the space-charge contribution dominates the potential variation within the extended SCL. Directly at the grain boundary core, segregation and atomic density related MIP changes dominate over the electrostatic potential of the SCL as discussed previously [30, 34] preventing a precise interpretation in terms of the electrostatic profile of the SCL.

Figure 5g shows the electrostatic potential, electric-field, and charge-density profiles reconstructed for the pure SCL model, which reproduce the main qualitative features observed experimentally. Figure 5h compares the experimental and simulated SCL electric-field profiles after normalization to the same peak amplitude. The overall field-reversal behavior and spatial characteristics of the extended SCL are similar, indicating that the model captures the main features of the measured electrostatic response. At the same time, differences near the grain-boundary core and in the detailed profile shape indicate that the measured response cannot yet be attributed uniquely to the space-charge field alone. Depending on the segregating species, the MIP gradient may either enhance or reduce the apparent DPC amplitude. Thus, reliable quantitative analysis of grain-boundary DPC data requires explicit consideration of both space-charge electrostatics and segregation-induced MIP variations. The present model does not represent the exact experimental grain-boundary type and does not account for possible surface-damage effects. Further studies separating SCL, MIP, projection, and possible charging contributions will be required for a fully quantitative

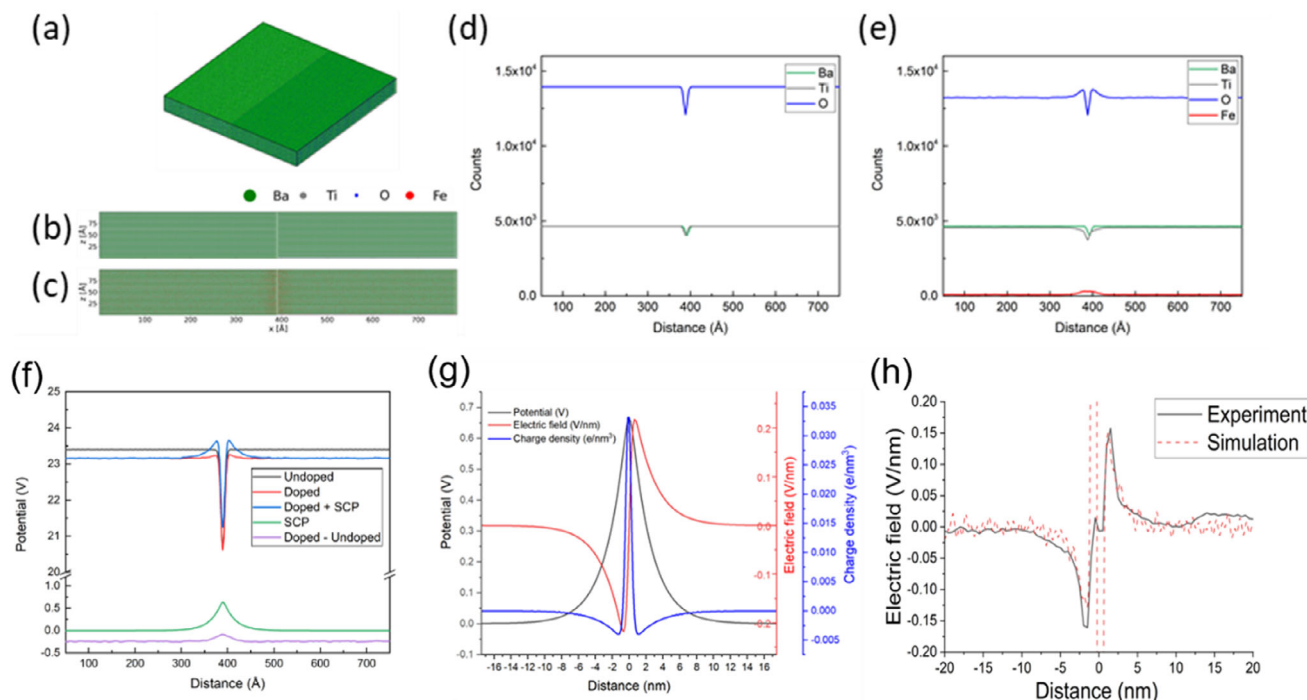


FIGURE 5 | Atomic structure and electrostatic analysis of a $\Sigma 5$ grain boundary in BaTiO_3 based on atomistic modeling. (a) Atomistic simulation cell of the grain-boundary model. (b,c) Atomic configurations of the grain-boundary region for the undoped and Fe-doped models. (d,e) Element-resolved atom counting profiles across the grain boundary for the undoped and the Fe-doped models. (f) Comparison of the mean inner potential (MIP) profiles for the undoped and doped models together with the space-charge potential, the combined potential, and the difference between the doped and undoped MIP profiles. (g) Electrostatic potential, electric-field, and charge-density profiles reconstructed for the pure SCL model across the grain boundary. (h) Comparison of the experimentally measured electric-field profile with the simulated space-charge electric-field profile, with both profiles normalized to the same peak amplitude for comparison.

interpretation. Beyond the intrinsic SCL and MIP contributions, several experimental factors limit absolute quantification. Residual field offsets can accumulate during potential integration, although vacuum-reference correction and relative referencing minimize this effect. Finite probe convolution broadens the grain-boundary-core response, whereas the approximately 0.5 nm probe remains sufficiently small to resolve the extended SCL. Uncertainty in Δz mainly affects the absolute field magnitude. Possible specimen, surface, or beam-induced charging cannot be fully separated and remains an additional uncertainty.

A key strength of the present approach is its capability for large-area correlative analysis in polycrystalline materials, directly combining crystallographic orientation mapping with electric-field, charge-density, and elemental-distribution measurements in the same region. The reduced crystallographic background provided by beam precession and edge-based disk-position analysis enables this correlative analysis. This is illustrated in Figure 6 for polycrystalline Fe-doped SrTiO_3 , which combines an ACOM orientation map with the corresponding DPC, reconstructed charge-density, and Fe-concentration maps. Both the DPC and charge-density maps show only weak variations within the grain interiors, whereas distinct interfacial signals are clearly resolved at the grain boundaries. The Fe map further reveals that dopant segregation is spatially heterogeneous and tends to be enhanced at selected interfaces. Line profiles extracted across two representative grain boundaries imaged close to edge-on conditions show that the reconstructed charge-density maxima

broadly coincide with Fe-enriched regions at the grain boundary, supporting a close correlation between local chemistry and electrostatic response.

The spatial correlation between Fe enrichment and reconstructed charge-density indicates that Fe segregation modifies the local defect equilibrium and electrostatic potential at the grain boundary, qualitatively in agreement with established SCL models [7]. In Fe-doped STO, segregated Fe can act as an acceptor-related defect center and lead to a redistribution of compensating defects, such as oxygen vacancies or charge states of acceptors. Such defect compensation and local charge transfer processes can contribute to the formation of a grain boundary potential barrier and thereby affect macroscopic electrical and ionic transport properties. The detailed profile shapes are not identical and, in some cases, exhibit pronounced asymmetry, suggesting that the local electrostatic behavior is influenced not only by segregation but also by the specific grain-boundary structure, projection effects, and possible charging or surface contributions. Such asymmetric profiles have been shown to depend on grain boundary migration during grain growth by phase-field simulations and are often observed at grain boundaries separating large and small grains [40, 45]. While a full statistical correlation analysis remains challenging, our new approach enables reliable measurement of electrostatic properties and their correlation with structural and chemical information in polycrystalline ceramics toward a more comprehensive understanding of complex non-conducting and semiconducting polycrystalline materials

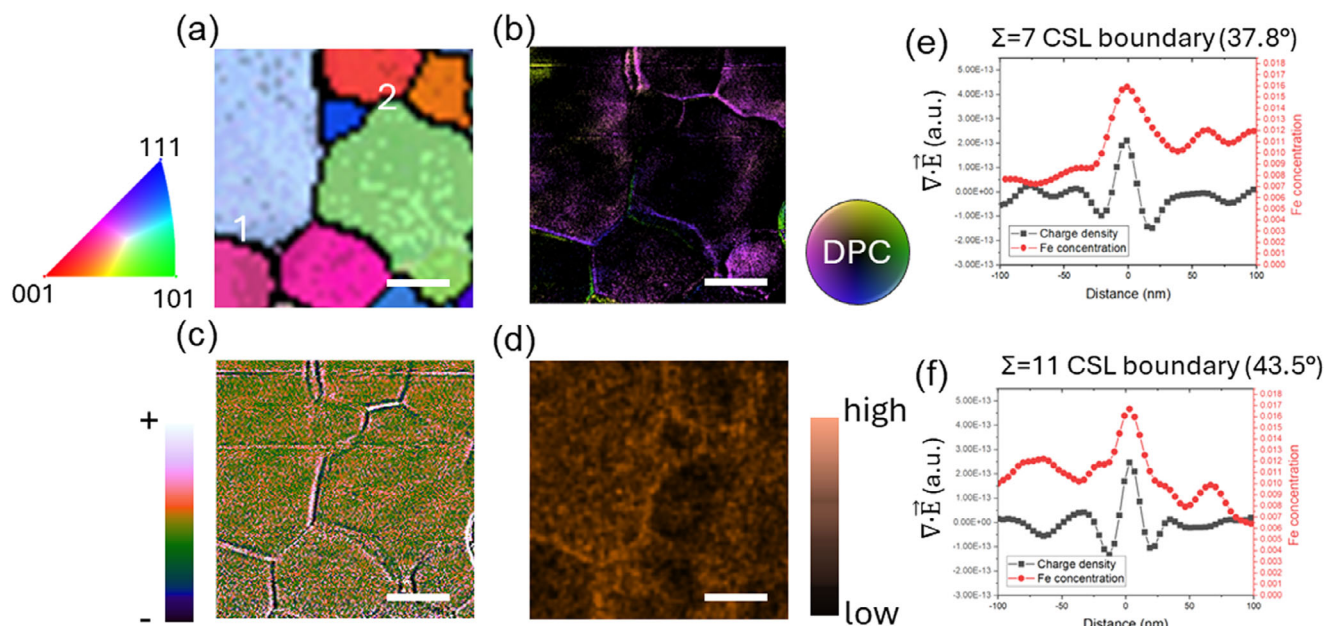


FIGURE 6 | Large-area correlative mapping of microstructure, DPC response, reconstructed charge density, and Fe distribution in polycrystalline Fe-doped SrTiO₃. (a) ACOM orientation map of the analyzed region, with the orientation color key shown on the left; the two grain boundaries selected for detailed analysis are labeled 1 and 2. (b) Corresponding large-area DPC map, with the DPC color wheel shown as a reference, revealing pronounced interfacial contrast at the grain boundaries. (c) Charge-density map reconstructed from the divergence of the DPC-derived electric field, showing localized electrostatic features at the grain boundaries while the grain interiors remain comparatively uniform. (d) Fe-concentration map of the same region, highlighting spatial variations in dopant segregation. (e) Line profile across grain boundary 1, comparing the reconstructed charge-density signal with the local Fe concentration. (f) Line profile across grain boundary 2, again comparing the reconstructed charge-density signal with the local Fe concentration. In both cases, the grain boundaries show distinct interfacial responses, and the charge-density maxima broadly coincide with Fe-enriched regions, although the detailed profile shape and asymmetry vary from one boundary to another. Together, these results demonstrate the utility of the present approach for large-area correlative analysis of electrostatic and chemical inhomogeneity in polycrystalline oxides. All scale bars correspond to 200 nm.

complementing indirect bulk measurements such as electrical impedance spectroscopy [42].

4 | Summary

We have demonstrated that precise large-area electric-field mapping of the space-charge layer around grain boundaries in polycrystalline oxides can be significantly improved by combining electron beam precession with SVD-based bright-field disk fitting in 4D-STEM. This combined approach significantly suppresses diffraction- and orientation-induced artifacts compared to conventional CoM-based analysis and enables more reliable extraction of DPC signals in structurally heterogeneous regions. Using this workflow, we obtained grain boundary resolved electric-field maps and further derived electrostatic potential and charge-density distributions from the measured field profiles for BaTiO₃ and SrTiO₃. Atomistic modeling of a Σ5 BaTiO₃ grain boundary supports the interpretation that the SCL electric field is the dominant contribution within the extended SCL, while segregation-induced mean-inner-potential gradients modify the apparent DPC response and must be considered for quantitative interpretation. Overall, this study provides an effective strategy for reliable electrostatic mapping in complex polycrystalline materials and extends the applicability of 4D-STEM DPC to the analysis of SCL related grain boundary phenomena.

Author Contributions

C.K. initiated and supervised the project. S.K. developed the methodology and performed the TEM and 4D-STEM experiments. S.K., H.C., M.T., X.M., J.K.L., M.S., K.A., and C.K. performed the simulations and analyzed the simulation results. S.K., H.C., A.R.N., Z.D., X.M., D.W., W.R., K.W., B.-X.X., A.K., and C.K. contributed to data analysis, interpretation, and scientific discussion. A.K. contributed to method development, sample provision, and interpretation of the electrostatic measurements. S.K. and C.K. wrote the original draft. All authors reviewed and edited the manuscript and approved the final version.

Acknowledgements

S.K. and C.K. greatly appreciate the discussions with Roger A. De Souza on space charge layers in oxide ceramics.

Funding Information

The authors express their gratitude to the Karlsruhe Nano Micro Facility (KNMF) for providing access to FIB and TEM facilities. S.K., H.C., W.R., K.W., B.-X.X., M.S., K.A., A.K., and C.K. acknowledge the support from collaborative research center FLAIR (Fermi level engineering applied to oxide electroceramics), which is funded by the German Research Foundation (DFG), project-ID 463184206 – SFB 1548. X. M. acknowledges financial support from the National Natural Science Foundation of China (127000-832011). This work was supported by the Technology Innovation Program (RS-2024-00418991) funded by the Ministry of Trade, Industry & Energy (MOTIE, Korea). Additionally, the authors appreciate the support received through the Federal Ministry of Education and Research

(BMBF) for the Innovation Pool Joint Lab Model Driven Materials Characterization (MDMC) and acknowledge backing from the Helmholtz Imaging Project (HIP) BRLEMM.

Conflicts of Interest

The authors declare no conflicts of interest.

Data Availability Statement

The data generated in this study are available at KITOpen at <https://doi.org/10.35097/7rmnd7w9mz4b1kb0> and are also available upon request from the authors.

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Supporting Information

Additional supporting information can be found online in the Supporting Information section.

Supporting File 1: smll75940-sup-0001-SuppMat.wmv.

Supporting File 2: smll75940-sup-0002-SuppMat.docx.