nature portfolio

Peer Review File

Direct observation of space-charge-induced electric fields at oxide grain boundaries

Corresponding Author: Professor Naoya Shibata

This file contains all reviewer reports in order by version, followed by all author rebuttals in order by version.

Version 0:

Reviewer comments:

Reviewer #1

(Remarks to the Author)
• What are the noteworthy results?
The authors note that there is a pressing need to observe space charge layers directly of individual grain boundaries as things like grain orientation, atomic structure, and chemistry and their effect on space charge layers. Previous studies have attempted this observation by TEM and STEM, but due to the effect of diffraction contrast interpretable and quantifiable results were difficult. Here they employ the technique of tilt-scan averaged differential phase contrast STEM (tDPC) which reduces the effect of diffraction contrast allowing the desired signal, an effect of the electromagnetic field at the SCL or crystal interface, to be clearly seen and quantifiably analyzed. Here they apply tDPC to YSZ oxide grain boundaries between two grains of the same orientation observed directly at an atomic scale. With this method they are able to observe the electric field lines across the grain boundary and along with chemical understanding from EDS, and observations of the atomic structure, they are able to build an understanding of what is occurring at the interface including how some impurities effect the SCL at the GB. They apply this to 4 different crystal orientations.
• Will the work be of significance to the field and related fields? How does it compare to the established literature? If the work is not original, please provide relevant references.
I believe this is work is significant. It is a novel use of the tDPC and the authors have demonstrated its effectiveness in mapping observed differences in the GB to changes in the shape and intensity of the SCL. It will allow, as the authors note, better fundamental understanding of the complex interplays of GB effects on SCLs, but this type of work could be useful for more broadly to materials where electric fields may be important. However, as other works have noted, this technique may not be as useful for Li-containing material since they tend to be more beam sensitive.
• Does the work support the conclusions and claims, or is additional evidence needed?
The work does support its conclusions. The STEM work clearly shows the interfaces in HAADF which is more readily interpretable. The EDS nicely shows some of the impurities in the GBs
• Are there any flaws in the data analysis, interpretation and conclusions? Do these prohibit publication or require revision?
No, the data was nicely demonstrated and appeared to be interpreted clearly.
• Is the methodology sound? Does the work meet the expected standards in your field?
Yes.
• Is there enough detail provided in the methods for the work to be reproduced?
The methods were nicely detailed for the STEM section, which is the bulk of the paper. However, I do think sample preparation is critical to reproduce something like this. It would have been nice for them to include the Ar ion-beam milling parameters, at least the final milling energy, as well as what was use for mechanical polish.
I did have a comment on Figure 1, it is beautifully illustrated, but it is unclear what the blue arrow on the detector is meant to be and whether it is related to the blue arrow that indicates the E field in the sample near the top of the figure. It appears to be indicating the direction of the shift of the beam on the detector due to the field, but that might be helpful to clarify.
I would have like to hear how they expected SCL like they observed might change across two grains of different orientations since all the GBs they examined were between grains of the same orientation. I suspect this was to help simplify the experiment, which I appreciated, it made the results more clearly identifiable, but many materials, if not most do not end up with such GBs, so how might it change for more realistic materials?
I also wondered if the authors had tried EELS to understand the coordination of the Y in the grain boundaries? There was some discussion about the atomic sites Y sits in, and understanding why Y segregates to those sites sounds interesting.

Reviewer #2

(Remarks to the Author)

Reviewer #3

(Remarks to the Author)
Toyama et al. examine space charge layers at grain boundaries in the oxide-ion conductor YSZ. Using tDPC STEM they determine the electric field profiles across a variety of bicrystal grain boundaries. The profiles are analysed with a simple space charge model.

The authors discuss problems with the tDPC STEM method and obtain some very impressive results. However, the analysis of results in a space charge model is too simplistic. They use a linear (!) model, although such a model is never used to describe the potential distribution at space charge layers (it is sometimes used to analyse resistances, but this is not what the authors require). In addition, they ignore the profiles of Y close to the interfaces in calculating the potential. Furthermore, the authors cite space charge models that treat oxides as dilute solutions of defects, whereas YSZ has 20 at% Y. This is particularly problematic because the authors use the analysis to discuss the origin of space charge layers. Since they use an incorrect analysis model, they will necessarily come to incorrect conclusions. (Abrupt oxygen vacancy profile is only expected for dilute solution, which is not the case for YSZ). The authors need to perform a much better analysis of their data. The TEM data deserve it.

To summarise: the TEM part is very good, but the analysis needs to be physically realistic and to take into account the defect chemistry of YSZ. As a consequence, I cannot recommend publication of the manuscript in its current state.

Further points for the authors to consider:
“direct observation of space charge layer”. Strictly speaking, in tDPC it is not the space charge layer that is observed. Direct observation would require the space charge to be examined, not the field. The authors need to correct the title and the text.

In this respect, direct observation has been made with TEM: Backhaus-Ricoult, Monika, Michael Badding, and Yves Thibault. "Grain boundary segregation and conductivity in yttria-stabilized zirconia." Advances in Electronic and Electrochemical Ceramics: Proceedings of the 107th Annual Meeting of The American Ceramic Society.

The authors write that “As a result, comprehensive understanding of SCLs at GBs still remains elusive.” This is not quite correct. And with regard to the manuscript, it does not correctly describe the contents.

In general, the manuscript should be improved so that the results are presented and discussed better.

Version 1:

Reviewer comments:

Reviewer #1

(Remarks to the Author)
All my concerns with the original manuscript have been addressed in the revision, and I am satisfied with the authors responses. I recommend the manuscript for publication.

Reviewer #2

(Remarks to the Author)
In the revised submission "rev1", The authors addressed my comments 1-7, but did not address 8-10.

Minor revision would be needed to prepare the present work for publication in Nature Communications.

Completed in submission rev1
1. This work demonstrates the correlation between SCLs and Y segregation, but it has not tracked change of oxygen and oxygen vacancies at GBs and what is the role of SCLs in distribution and concentration of oxygen vacancies, which may be a crucial factor for oxygen ionic conduction. I suggest including a discussion of the oxygen mapping and/or quantification data (from their prior publication) in the context of impurity segregation.
2. At Line 136, this work mentions ‘there can be a dip in the mean inner potential along the GB core even though the GB is not charged.’ Could you please explain more in detail for this point? And are there any references that support this point?
3. Do impurities, like Al and Si, affect segregation of Y3+ , core charge and SCLs?
4. Move the EDS in the main text figure, and include the quantification of Al, Si in Table 1 and discuss the correlation between Si and Al concentrations with SCL.
5. Plot SCL for each GB in main text (experimental potentials should look like fig. 4c according to the authors’ manuscript). This will also support their claim that it is “possible to directly and quantitatively characterize SCLs at individual GBs.” Important to the goal of quantitatively characterizing the SCL is showing the spatial distribution of the SCL.

6. Fig. S2 should indicate these are EDS signal intensity maps, and any image processing/filtering applied to the data.
7. It appears that Y segregation was clearly detected at specific GB atomic sites in the Sig5(001)/(210) as well, this should be stated near line 110.

Not addressed in submission rev1
8. In addition to the driving forces discussed, how is segregation affected by the local oxygen non-stoichiometry. What are the effects of defect chemical (i.e., defect interactions and charge compensation) interactions near the GB?
9. Line 135 should specify that “the thickness of GB is often thinner than the bulk regions due to the selective etching by” is referring to the TEM specimen thickness in the direction parallel to the beam.
10. Provide your estimates of space charge widths.

Reviewer #3

(Remarks to the Author)
The authors are to be congratulated on improving the manuscript substantially. A few minor points remain concerning the origin of the core charge:

#1. Line 235: this needs to be the difference in the standard chemical potential of oxygen vacancies. In addition, Ref. 11 does not mention this. Better references here are perhaps:
https://doi.org/10.1016/0167-2738(94)00184-T
https://doi.org/10.1016/j.ssi.2004.07.052

#2. The abrupt concentration change in vacancy concentration in the core is only the case for a dilute solution. If the authors use a Poisson-Cahn model, this is no longer true. Please correct the text.

#3. The broken-bond mechanism is problematic for an ionic material because there are no bonds to be broken. I think it is worth mentioning the model, but it should be discussed critically.

Version 2:

Reviewer comments:

Reviewer #2

(Remarks to the Author)
My comments were addressed.

Reviewer #3

(Remarks to the Author)
I am satisfied with the authors responses. I am happy to recommend the manuscript for publication.

RESPONSE TO REVIEWERS' COMMENTS

Response to the Reviewer #1

We thank the reviewers for reviewing our manuscript. We are very gratified that the reviewer agrees with us on the significance of our findings. The reviewer raised several questions and comments on our manuscript. We have carefully considered all the comments raised by the referee, and revised out manuscript accordingly by incorporating new discussion, in order to answer all these comments. The summary of our responses to the points raised by the reviewer and the corresponding changes made to the manuscript are italicized and interspersed between the reviewer's report below. In the revised manuscript, we highlight how we revised our manuscript by red color font.

· What are the noteworthy results?

The authors note that there is a pressing need to observe space charge layers directly of individual grain boundaries as things like grain orientation, atomic structure, and chemistry and their effect on space charge layers. Previous studies have attempted this observation by TEM and STEM, but due to the effect of diffraction contrast interpretable and quantifiable results were difficult. Here they employ the technique of tilt-scan averaged differential phase contrast STEM (tDPC) which reduces the effect of diffraction contrast allowing the desired signal, an effect of the electromagnetic field at the SCL or crystal interface, to be clearly seen and quantifiably analyzed. Here they apply tDPC to YSZ oxide grain boundaries between two grains of the same orientation observed directly at an atomic scale. With this method they are able to observe the electric field lines across the grain boundary and along with chemical understanding from EDS, and observations of the atomic structure, they are able to build an understanding of what is occurring at the interface including how some impurities effect the SCL at the GB. They apply this to 4 different crystal orientations.

· Will the work be of significance to the field and related fields? How does it compare to the established literature? If the work is not original, please provide relevant references.

I believe this is work is significant. It is a novel use of the tDPC and the authors have demonstrated its effectiveness in mapping observed differences in the GB to changes in the shape and intensity of the SCL. It will allow, as the authors note, better fundamental understanding of the complex interplays of GB effects on SCLs, but this type of work could be useful for more broadly to materials where electric fields may be important.

Response:

We are gratified that the reviewer agreed with us on the novelty and importance of our paper.

However, as other works have noted, this technique may not be as useful for Li-containing material since they tend to be more beam sensitive.

Response:
The dose conditions employed in the current tDPC experiments are comparable to the condition for observing Li-containing materials (Lin et al. Sci Rep 4, 5694 (2014)). Thus, we believe that our method could be also useful in such research field in the future.

In the revised manuscript, we have added the information on the electron dose conditions in the Method section, along with the following sentences in the Main section.

Reference:
(Ref. 53) Lin F, et al. Sci Rep 4, 5694 (2014).

(Line 308)
The probe current, dwell time, and probe size were set to be approximately 12 pA, 98 µsec/pixel and 0.7 nm, respectively. The electron dose with these conditions is estimated to be about 2000 $e^-/Å^2$.
(Line 259)
Furthermore, given the present dose condition detailed in the Method, tDPC STEM observations reported here hold potential for observing more beam-sensitive materials such as Li-battery materials[53]. The present technique may lead to our general understanding of grain boundary resistivity in many types of ion-conductors.

· Does the work support the conclusions and claims, or is additional evidence needed?
The work does support its conclusions. The STEM work clearly shows the interfaces in HAADF which is more readily interpretable. The EDS nicely shows some of the impurities in the GBs
· Are there any flaws in the data analysis, interpretation and conclusions? Do these prohibit publication or require revision?
No, the data was nicely demonstrated and appeared to be interpreted clearly.
· Is the methodology sound? Does the work meet the expected standards in your field?
Yes.
· Is there enough detail provided in the methods for the work to be reproduced?
The methods were nicely detailed for the STEM section, which is the bulk of the paper.

However, I do think sample preparation is critical to reproduce something like this. It would have been nice for them to include the Ar ion-beam milling parameters, at least the final milling energy, as well as what was use for mechanical polish.

Response:
In revised manuscript, we have added the following sentence on TEM sample preparation in the Method section.

(Line 287)
TEM specimens were prepared via mechanical polishing using 9 to 1 μm diamond suspensions followed by Ar ion-beam thinning using 3.5kV to 0.5 kV accelerating voltages.

I did have a comment on Figure 1, it is beautifully illustrated, but it is unclear what the blue arrow on the detector is meant to be and whether it is related to the blue arrow that indicates the E field in the sample near the top of the figure. It appears to be indicating the direction of the shift of the beam on the detector due to the field, but that might be helpful to clarify.

Response:
We appreciate the reviewer's suggestion. We clarify the meaning of blue arrow as "Coulomb deflection" in Fig. 1.

I would have like to hear how they expected SCL like they observed might change across two grains of different orientations since all the GBs they examined were between grains of the same orientation. I suspect this was to help simplify the experiment, which I appreciated, it made the results more clearly identifiable, but many materials, if not most do not end up with such GBs, so how might it change for more realistic materials?

Response:
As the reviewer noted, we employed well-defined symmetric tilt GBs, which were fabricated by bicrystal method. It is possible that, in asymmetric GBs, the charges may appear asymmetrically across the GBs, possibly due to the differences in diffusion coefficients of ions along different crystal orientations.
In addition, our results indicate that space charge is strongly dependent on the atomic structures of the GB cores. If we attribute this origin to be the disruption of atomic bonds within the GB cores, it is possible that larger space charge layers may appear at

asymmetric or random grain boundaries, which typically have more disordered core atomic structures. Investigating more realistic grain boundaries with the present technique will be our future work.

We have added the following sentences on these points in the revised manuscript as follows.

(Line 255)
In polycrystalline materials, asymmetric or random grain boundaries, which often have more disordered core atomic structures, might have larger space charge. Investigating such more realistic grain boundaries using the present technique will be our future work.

I also wondered if the authors had tried EELS to understand the coordination of the Y in the grain boundaries? There was some discussion about the atomic sites Y sits in, and understanding why Y segregates to those sites sounds interesting.

Response:
Some previous studies, for example, those by Lei et al. 2002 and Backhaus-Ricoult et al. 2005 (Reviewer 3 suggested), have performed EELS measurements at YSZ GBs. These studies observed yttrium segregation at GBs, similar to our results. However, the EELS spectrum in YSZ is typically less sensitive to the coordination of yttrium, making quantitative interpretation very challenging (Lei et al. 2002).
Regarding the reasons of yttrium segregation, two possible causes have been suggested (Feng et al. 2016 and 2017): the elastic effect due to the difference in ionic radius between yttrium and zirconium, and the electrostatic effect due to space charges. Previously, the direct evidence for the electrostatic effect was totally lacking. Our current results thus show a clear and direct correlation between space charges and the yttrium segregation for the first time, strongly suggesting the presence of the electrostatic effect for segregation.

References:
(Ref. 22) Lei et al. Journal of the American Ceramic Society 85, 2359 (2002).
(Ref. 21) Backhaus-Ricoult et al. Proceedings of the 107th Annual Meeting of The American Ceramic Society *(2005).*
(Ref. 37) Feng et al. Nat. Commun. 7, 11079 (2016).
(Ref. 38) Feng et al. ACS Nano 11, 11376-11382 (2017).

We have added the following sentences in the revised manuscript.

(Line 67)

In addition, while some studies have attempted to measure SCs with STEM-electron energy loss spectroscopy (EELS)[21, 22]in terms of the chemical change, the sensitivity of the STEM-EELS spectrum in YSZ is typically insufficient to detect subtle changes in oxygen vacancy distribution or Yttrium coordination.

Response to the Reviewer #2

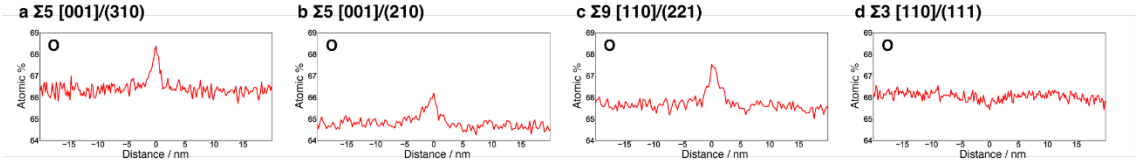
We thank the reviewers for reviewing our manuscript. The reviewer raised several questions and comments on our manuscript. We have carefully considered all the comments raised by the referee, and revised out manuscript accordingly by incorporating new discussion, in order to answer all these comments. The summary of our responses to the points raised by the reviewer and the corresponding changes made to the manuscript are italicized and interspersed between the reviewer's report below. In the revised manuscript, we highlight how we revised our manuscript by red color font.

1. This work demonstrates the correlation between SCLs and Y segregation, but it has not tracked change of oxygen and oxygen vacancies at GBs and what is the role of SCLs in distribution and concentration of oxygen vacancies, which may be a crucial factor for oxygen ionic conduction. I suggest including a discussion of the oxygen mapping and/or quantification data (from their prior publication) in the context of impurity segregation.

Response:

The oxygen concentration changes were reported in our previous studies. We here show oxygen line profiles (atomic %) for each GB from our previous publications (Feng et al. 2016, 2017). These profiles show clear increase of oxygen concentration particularly at the Σ5(310) and Σ9 (221) GBs, and some extent at the Σ5(210). These results indirectly suggested the presence of space charges at these GBs since the accumulation of negatively charged Y_{Zr} and the depletion of positively charged V_O are simultaneously occurred at the GBs. However, as electron beam channeling severely affects the quantification of GB oxygen content by STEM EDS (Feng et al. 2017, 2018), it is still challenging to discuss the quantitative GB oxygen content by STEM EDS.

Given these considerations, our results of direct and quantitative observations of electric fields and associated charges across GBs should be more suitable and powerful to discuss intricate nature of GB SCLs in those ionic crystals.



Line profiles of O concentration (atomic %) across the ∑5[001](310), ∑5[001](210),

∑9[110]/(221) and, ∑3[110]/(111) GBs (Feng et al. 2016, 2017).

References:
(Ref. 37) Feng et al. Nat Commun 7, 11079 (2016).
(Ref. 38) Feng et al. ACS Nano 11, 11376-11382 (2017).

We have added the following discussion on oxygen concentration.

(Line 203)
The negative charges observed around the GBs suggest the depletion of positively charged oxygen vacancies in these regions. From the previous studies, oxygen ions were shown to strongly segregate at the ∑5[001]/(310), ∑9[110]/(221) and slightly segregate at the ∑5[001]/(210) GBs, but not to segregate at the ∑3[110]/(111) GB[37, 38]. These findings are consistent with our tDPC experiments, which indicate the amount of SC differes as ∑9[110]/(221) ≈ ∑5[001]/(310) > ∑5[001]/(210) > ∑3[110]/(111).

2. At Line 136, this work mentions 'there can be a dip in the mean inner potential along the GB core even though the GB is not charged.' Could you please explain more in detail for this point? And are there any references that support this point?

Response:
Mean inner potential (MIP) is defined as a volume average of atomic potential of the specimen (Sanchez et al. 1985, O'Keeffe and Spence 1994). By its definition, MIP is sensitive to the variation of atomic density and thickness within the specimen. These variations result in the generation of DPC signals in addition to the DPC signals by charge distribution (Wu et al. 2017). It is commonly observed that atomic density decreases at GB cores, resulting in the drops of MIP (Rühle et al. 2006, Rajak et al. 2015), which is similar to our study.

References:
(Ref. 41) Sanchez et al. Solid State Physics 18, 33-41 (1985)
(Ref. 43) O'Keeffe et al. Acta Crystallographica Section A 50, 33-45 (1994)
(Ref. 44) Wu et al. Ultramicroscopy 176, 233-245 (2017)
(Ref. 45) Rühle et al. Philosophical Magazine A 49, 759-782 (2006)
(Ref. 46) Rajak et al. Journal of Materials Science 51, 1484-1489 (2015)

We have added the following sentences and references in the revised manuscript to clarify these points.

(Line 137)

Mean inner potential (MIP), which is defined as a volume average of atomic potential of the specimen, can affect DPC signal in addition to the electric fields originated from charge distribution[41, 42, 43, 44]. Since the local atomic density of the GB core is often intrinsically lower than that of the bulk and the thickness of GB core is often thinner than the bulk regions due to the selective etching by ion milling, there can be a dip in the MIP along the GB core. The local gradient in MIP results in an electric field, which produces DPC signal, even though the GB were not charged and without charge distribution [45,46].

3. Do impurities, like Al and Si, affect segregation of Y3+ , core charge and SCLs?

Response:

If Si substitutes for Zr sites at the GB cores, it should not alter formal charges at these sites. On the other hand, if Al substitutes Zr at the GB cores, it should cause negative formal charges. Additionally, if these impurities occupy interstitial sites at the GB cores, they should cause positive charges. Therefore, these impurities could potentially affect the GB core charges and SCLs as discussed in the manuscript.

We clarified these points more clearly by adding the following sentences in the revised manuscript.

(Line 242)

If Si substitutes for Zr sites at the GB cores, no formal charge should be formed at these sites. On the other hand, if Al substitutes for Zr at the GB cores, negative formal charges should be formed. Moreover, if these impurities occupy interstitial sites at the GB cores, positive charges should be formed.

4. Move the EDS in the main text figure, and include the quantification of Al, Si in Table 1

and discuss the correlation between Si and Al concentrations with SCL.

Response:
We have moved the EDS data from Supplementary materials to the main text and have added the quantitative values for low-mag EDS mappings of Al and Si in Table 1. However, as quantification of atomic-resolution EDS is challenging due to the electron channeling effect (Chen et al. 2017), it is difficult to accurately quantify the concentration of substituted impurities and interstitial impurities from the atomic-resolution EDS at the present stage. As discussed above, the effect of Si and Al on space charge can vary depending on whether they are in interstitial or Zr sites, it is therefore difficult to simply discuss the correlation between these defect concentrations with SCLs.

Reference:
(Ref. 52) Chen et al. Ultramicroscopy 176, 52-62 (2017).

We have added the following sentences in the revised manuscript.

(Line 247)
Although the atomic-resolution Si and Al EDS maps suggest that the segregated impurity atoms may occupy both Zr sites and interstitial sites at the GB cores (Fig. 3), quantifying charge amount by such impurities remains highly challenging due to the electron channeling effect in atomic-resolution EDS mapping[52].

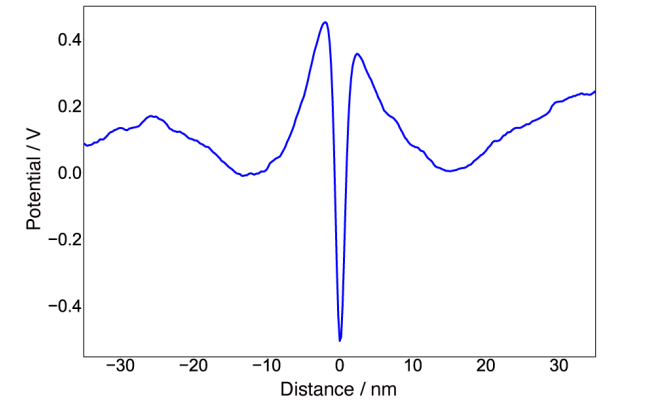
5. Plot SCL for each GB in main text (experimental potentials should look like fig. 4c according to the authors' manuscript). This will also support their claim that it is "possible to directly and quantitatively characterize SCLs at individual GBs." Important to the goal of quantitatively characterizing the SCL is showing the spatial distribution of the SCL.

Response:
The electric field and potential caused by SC, which satisfy the Poisson equation, physically describe the same phenomena, except for the zero point of potential. In DPC STEM, we directly measure electric field distributions. These distributions can be converted into electrostatic potentials mathematically through the integral process of DPC signals via setting boundary conditions (Ishizuka et al. 2017). A potential profile of the Σ5(310) GB obtained via this integral process of the tDPC STEM electric field is shown below, and the resultant profile basically agrees with the potential shown in Fig. 6c in the revised manuscript. However, this mathematical operation can enhance artefacts,

particularly due to low-frequency noise, as discussed in our previous publication (Toyama et al. 2023).
Therefore, we present electric field profiles as our main data. It is important to emphasize that the observed divergent electric field distributions are intrinsically equivalent to the positive potential caused by positive charge at the core and negative space charge around GB.

References:
(Ref. 30) Toyama S. et al. Nature Nanotechnology 18 521 (2023).
(Ref. 57) Ishizuka A. et al. Microscopy 66 397 (2017).

We added the potential profile as shown below in the supplementary figure. Considering all these facts and following the Reviewer 3's suggestion, we have changed the title of the paper to "Direct observation of space-charge-induced electric fields at oxide grain boundaries".



Supplementary Fig. S1 Potential profile of the ∑5[001]/(310) grain boundary obtained through the integral process of tDPC STEM experiment. Although the profile contains low-frequency artefacts by the integral process[30], it basically agrees with the space charge potential profile schematically shown in Fig. 6c.

6. Fig. S2 should indicate these are EDS signal intensity maps, and any image processing/filtering applied to the data.

Response:
Fig. S2 (and Fig. 4 in the revised manuscript) is the cation ratio map calculated using

EDS signals.

We have added the following information about Fig. 4 in the Method.

(Line 297)
Low magnification two-dimensional EDS maps were taken at all the GBs. Then, the line profiles across the GBs are formed by integrating the EDS signal parallel to the GBs to obtain quantitative amount of segregation (Fig.4 and Table1). The GB chemistry was defined by the cation ratio, namely N_i/N_{total}, where N_i is the number of atoms for cation i and N_{total} is the total number of cations.

7. It appears that Y segregation was clearly detected at specific GB atomic sites in the Sig5(001)/(210) as well, this should be stated near line 110.

Response:
As the reviewer noted, the Σ5(210) GB has relatively stronger Y segregation sites. It is possible that the elastic energy may contribute to Y segregation to the specific sites in the Σ5(210) GB core.

We had added the following sentences in the revised manuscript.

(Line 114)
In addition, Y segregation was clearly detected at specific GB atomic sites in the ∑3[110]/(111) and partially in the ∑5[001]/(210) GBs.

(Line 225)
At the ∑5[001]/(210) GB, while some preferential segregation sites were observed, Y segregation in total is less than the ∑5[001]/(310) and ∑9[110]/(221) GBs, suggesting that elastic energy may also affect the Y segregation at specific sites of the ∑5[001]/(210) GB core.

Response to the Reviewer #3

We thank the reviewers for reviewing our manuscript. We are very gratified that the reviewer agrees with us on the significance of our experimental results. The reviewer raised several questions and comments on our manuscript. We have carefully considered all the comments raised by the referee, and revised out manuscript accordingly by incorporating new discussion, in order to answer all these comments. The summary of our responses to the points raised by the reviewer and the corresponding changes made to the manuscript are italicized and interspersed between the reviewer's report below. In the revised manuscript, we highlight how we revised our manuscript by red color font.

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The authors discuss problems with the tDPC STEM method and obtain some very impressive results. However, the analysis of results in a space charge model is too simplistic. They use a linear (!) model, although such a model is never used to describe the potential distribution at space charge layers (it is sometimes used to analyse resistances, but this is not what the authors require). In addition, they ignore the profiles of Y close to the interfaces in calculating the potential. Furthermore, the authors cite space charge models that treat oxides as dilute solutions of defects, whereas YSZ has 20 at% Y. This is particularly problematic because the authors use the analysis to discuss the origin of space charge layers. Since they use an incorrect analysis model, they will necessarily come to incorrect conclusions. (Abrupt oxygen vacancy profile is only expected for dilute solution, which is not the case for YSZ). The authors need to perform a much better analysis of their data. The TEM data deserve it.

To summarise: the TEM part is very good, but the analysis needs to be physically realistic and to take into account the defect chemistry of YSZ. As a consequence, I cannot recommend publication of the manuscript in its current state.

Response:

We thank the reviewer for the important comments. We modified the fitting procedure as follows.

In the previous manuscript, we referred to the 'Mott-Schottkey model with linearized

depletion approximation' (Tong et al. 2019) as 'Linear model', which may lead to misunderstandings. Because this model allows for analytical solution: a potential that is a quadratic function of distance, it has been employed in several previous studies (Guo and Waser 2006, Xu et al. 2020). However, as the reviewer suggested, this model assumes a dilute solution, which may not be accurate for the cubic YSZ with 10 mol% Y_2O_3. Therefore, we have changed our fitting model to the Poisson-Cahn model (Mebane and De Souza 2015, Tong et al. 2019). The Poisson-Cahn model combines the Poisson-Boltzmann equation with the Cahn-Hilliard model (Cahn and Hilliard 1958), incorporating chemical interactions of point defects. This approach is suitable even in a high-dopant situation. Below, we present the results of fitting the Poisson-Cahn model to the experimental electric field at the ∑5[001]/(310) GB, and we have revised Table 1, accordingly.

References:

(Ref. 47) Tong X et al. Journal of the American Ceramic Society 103, 5-22 (2019).
(Ref. 11) Guo X and Waser R Progress in Materials Science 51, 151-210 (2006).
(Ref. 19) Xu X, et al. Nat Mater 19, 887-893 (2020).
(Ref. 33) Mebane DS and De Souza RA. Energy & Environmental Science 8, 2935 (2015)
(Ref. 48) Cahn JW and Hilliard JE The Journal of chemical Physics 28, 258 1958.

In the revised manuscript, we have included the following sentences.

(Line 165)

Here, we fitted the electric field line profiles obtained via the tDPC STEM experiment shown in Fig. 7 using a Poisson-Cahn model[33, 47]. The Poisson-Cahn model can describe space charge over the entire Y_2O_3 concentration range, from dilute to high dopant concentrations. This model combines the Poisson-Boltzmann equation with Cahn-Hilliard theory, incorporating chemical interactions of point defects. Within the Cahn-Hilliard framework[48], the electrochemical potentials of the acceptor dopant λ_a and oxygen vacancy λ_v are described as follows[33]:

$$\lambda_a = f_{aa} n_a(x) + f_{av} n_v(x) + k_B T \ln \frac{n_a(x)}{1 - n_a(x)} - e\phi(x) - \beta_a \frac{d^2 n_a(x)}{dx^2} \quad (1)$$

$$\lambda_v = f_{vv} n_v(x) + f_{av} n_a(x) + k_B T \ln \frac{n_v(x)}{1 - n_v(x)} + 2e\phi(x) - \beta_v \frac{d^2 n_v(x)}{dx^2} \quad (2)$$

where $\phi(x)$ is the electrostatic potential, $n_a(x)$ and $n_v(x)$ are the site fractions of the

acceptor dopant and oxygen vacancy, respectively, f_{ij} is the interaction energy between the species i and j, and β_i is the gradient energy coefficient for species i. The electrostatic potential $\phi(x)$ follows the Poisson's equation,

$$\varepsilon_r \varepsilon_o \nabla^2 \phi(x) = e\left(2N_v^b n_v(x) - N_a^b n_a(x)\right) \quad (3)$$

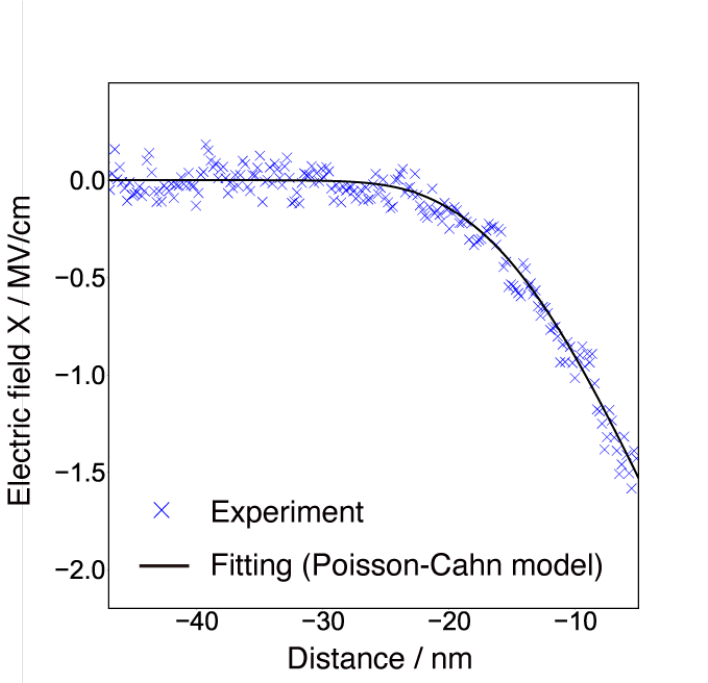
where ε_r and ε_o are the relative and vacuum permittivities, respectively, and N_i^b is the bulk site density of the species i. Boundary conditions for species i can be formulated from the mathematical variational analysis of free energy functional[49]:

$$N_i^b \beta_i \left.\frac{dn_i(x)}{dx}\right|_{x=0} = N_i^{GB} \eta_i^{GB} \quad (4)$$

where N_i^{GB} is the site density at the GB, and η_i^{GB} is the segregation energy. These equations can be numerically solved using the standard method. We calculated such Poisson-Cahn potential and electric field via Newton-Raphson method, as per the previous studies[32, 47]. The parameters of f_{ij}, β_i, and η_i^{GB} were optimized to fit the experimental electric fields. Although structurally induced mean inner potential decrease at the cores is superimposed in the electric field profiles (Fig. 7), we can quantify the space charge using the divergent electric field regions around the GBs. Details of the fitting procedure are shown in the Method.

(Line 320)

SCs and potentials were quantified by fitting the experimental electric field profiles to the electric field profiles of Poisson-Cahn model. We numerically calculated the Poisson-Cahn electric field by solving Eq. (1-4) via Newton-Raphson method according to the MATLAB script in the previous study[33]. The calculated electric field profiles were adjusted to match the experimental electric field profiles using cubic spline interpolation, and the parameters of f_{ij}, β_i, and f_i^{GB} in Eq. (1-4) were optimized using the Nelder-Mead method to minimize the squared error between the experimental and model electric fields.



Results of fitting the Poisson-Cahn model to the experimental electric field at the ∑5[001]/(310) grain boundary.

Further points for the authors to consider:

"direct observation of space charge layer". Strictly speaking, in tDPC it is not the space charge layer that is observed. Direct observation would require the space charge to be examined, not the field. The authors need to correct the title and the text.

Response:

We agree with the reviewer that the primary data is indeed the electric field. Therefore, we have revised the title to "Direct observation of space-charge-induced electric fields at oxide grain boundaries" to reflect our findings more accurately.

In this respect, direct observation has been made with TEM: Backhaus-Ricoult, Monika, Michael Badding, and Yves Thibault. "Grain boundary segregation and conductivity in yttria-stabilized zirconia." Advances in Electronic and Electrochemical Ceramics: Proceedings of the 107th Annual Meeting of The American Ceramic Society.

Response:

We thank the reviewer for the recommendation of the reference, and we have carefully examined the paper. In this paper, EELS analysis was performed to detect the

oxygen/dopant concentrations and valence states. Although EELS is a powerful technique to discuss chemical composition and local electronic structure, GB space charge itself was not directly observed, but only indirectly discussed based on the GB oxygen K-edge spectra. Furthermore, it is difficult to use EELS to detect subtle changes in oxygen vacancy concentrations around GBs. Consequently, detailed charge distributions at individual GBs have not been obtained. On the other hand, in this study, we directly observed electric field distributions caused by space charges at GBs. We believe our method provides a direct analysis of detailed charge distributions around GBs.

Reference:
(Ref. 21) Backhaus-Ricoult et al. Proceedings of the 107th Annual Meeting of The American Ceramic Society *(2005).*

We added the discussion on EELS with references in the revised manuscript.

(Line 67)
In addition, while some studies have attempted to discuss the SC with STEM-electron energy loss spectroscopy (EELS)[21, 22] in terms of the chemical change, the sensitivity of the STEM-EELS spectrum in YSZ is typically insufficient to detect subtle changes in oxygen vacancy distribution or Yttrium coordination.

The authors write that "As a result, comprehensive understanding of SCLs at GBs still remains elusive." This is not quite correct. And with regard to the manuscript, it does not correctly describe the contents.

Response:
We appreciate the reviewer's suggestion. We have revised the manuscript to reflect the current understanding more accurately.
(Line 70)
As a result, the detailed distribution and origin of SCLs at individual GBs still remain elusive.

In general, the manuscript should be improved so that the results are presented and discussed better.

Response:

We thank the reviewer again for the important comments, and hope you agree with our responses.

RESPONSE TO REVIEWERS' COMMENTS

Response to the Reviewer #1

We thank the reviewer for reviewing our revised manuscript.

All my concerns with the original manuscript have been addressed in the revision, and I am satisfied with the authors responses. I recommend the manuscript for publication.

Response:
We are very gratified that the reviewer now recommends our manuscript for publication in Nature Communications.

Response to the Reviewer #2

We thank the reviewer for reviewing our revised manuscript. We have carefully considered all the remaining concerns by the reviewer. In the following, we have addressed all the concerns and revised our manuscript accordingly by incorporating new discussions.

In the revised submission "rev1", The authors addressed my comments 1-7, but did not address 8-10. Minor revision would be needed to prepare the present work for publication in Nature Communications.

In addition to the driving forces discussed, how is segregation affected by the local oxygen non-stoichiometry. What are the effects of defect chemical (i.e., defect interactions and charge compensation) interactions near the GB?

Response:

Defect chemistry near the GB is governed by electric interaction between positively charged GB core and charged defects. Y_{Zr} has a negative formal charge and oxygen vacancy has a positive formal charge. Therefore, positively charged GB cores would attract Y_{Zr} and repel oxygen vacancy near the GB, to keep the charge neutrality. Such interaction would result in a GB Y segregation and oxygen vacancy depletion.

We have added the discussion of the detailed segregation mechanism in the revised manuscript.

(Line 231)

Positively charged GB cores would attract Y_{Zr} and repel oxygen vacancy near the GB. Such interaction would result in a GB Y segregation and oxygen vacancy depletion.

Line 135 should specify that “the thickness of GB is often thinner than the bulk regions due to the selective etching by” is referring to the TEM specimen thickness in the direction parallel to the beam.

Response:

We revised our manuscript to clearly describe the effect of selective etching.

(Line140)

Since the local atomic density of the GB core can be intrinsically lower than that of bulk, and the TEM sample thickness along the electron beam direction at GBs is often thinner than the bulk regions due to the selective etching by ion milling, there can be a dip in the MIP along the GB core.

Provide your estimates of space charge widths.

Response:
We thank the reviewer for this suggestion. We have added the estimation of space charge widths in the revised manuscript.

(Line 165)
Therefore, the widths of SCLs can also be estimated to be about 15 nm, based on the measured width of the divergent electric fields.

Response to the Reviewer #3

We thank the reviewer for reviewing our revised manuscript. We are gratified that the reviewer highly evaluated our previous revision. We further revised our manuscript in accordance with the new comments and suggestions as follows.

The authors are to be congratulated on improving the manuscript substantially. A few minor points remain concerning the origin of the core charge:
#1. Line 235: this needs to be the difference in the standard chemical potential of oxygen vacancies. In addition, Ref. 11 does not mention this. Better references here are perhaps:
https://doi.org/10.1016/0167-2738(94)00184-T
https://doi.org/10.1016/j.ssi.2004.07.052

Response:
We thank the reviewer for recommending the references. We have added the suggested references (Jamnik et al. 1995 and Tschope et al. 2004) in Line 243 in the discussion regarding the difference in the standard chemical potential of oxygen vacancies.

(References)
(Ref. 50) Jamnik et al. Solid State Ionics 75 51-58 (1995).
(Ref. 51) Tschope et al. Solid State Ionics 173 57-61 (2004).

(Line 236)
The origin of the positive core charges in YSZ GBs has conventionally been explained by the difference in the standard chemical potential of oxygen vacancies at the GB core and that within the grains[50, 51].

#2. The abrupt concentration change in vacancy concentration in the core is only the case for a dilute solution. If the authors use a Poisson-Cahn model, this is no longer true. Please correct the text.

Response:
We thank the reviewer for the suggestion. We have changed the description of oxygen vacancy distribution to reflect this correction.

(Line 239)

In this scenario, oxygen vacancies gradually accumulate to the GB core. The oxygen distribution has been studied in detail in our previous report[38]. STEM EDS in that study did not detect such oxygen vacancy accumulation in those GBs[38].

#3. The broken-bond mechanism is problematic for an ionic material because there are no bonds to be broken. I think it is worth mentioning the model, but it should be discussed critically.

Response:
The term 'broken-bond mechanism' used in the previous manuscript might have been misleading. In ionic materials, if the coordination of anion-cation is deficient at defects like grain boundaries, excess charges may be produced (Gracer et al. 2010 and Shibata et al. 2007). We propose that such a coordination deficient model could be the origin of the core charge at YSZ GBs. We have revised the manuscript to clearly describe the coordination deficient model.

References:
(Ref. 53) Gracer et al. Nature Physics 6, 609-614 (2010).
(Ref. 54) Shibata et al. Science 316, 82-85 (2007).

(Line 241)
Other mechanisms of positive core charges have been also proposed, including the existence of unintentional impurities such as Si or Al[18, 52], or non-stoichiometric anion-cation coordination deficiencies at the GB cores[53, 54]
(Line 255)
These results may still support the coordination deficient mechanism as the origin of the positive core charges. As the coordination environment at GB is often much different from those within the bulk, our conclusion could be applicable to those general GBs inside practical polycrystalline materials.