# Controlling grain boundary segregation to tune the conductivity of ceramic proton conductors

Moritz Kindelmann<sup>1,2</sup>, Ivan Povsturgar<sup>1</sup>, Severin Kuffer<sup>2</sup>, Dylan Jennings<sup>1,2,3</sup>, Julian N. Ebert<sup>3</sup>, Moritz L. Weber<sup>4</sup>, M. Pascal Zahler<sup>3</sup>, Sonia Escolastico<sup>5</sup>, Laura Almar<sup>5</sup>, Jose M. Serra<sup>5</sup>, Payam Kaghazchi<sup>2,6</sup>, Martin Bram<sup>2</sup>, Wolfgang Rheinheimer<sup>3</sup>, Joachim Mayer<sup>1,7</sup>, <u>Olivier Guillon<sup>2,8</sup></u>

<sup>1</sup> Forschungszentrum Jülich GmbH, Ernst Ruska-Centre for Microscopy and Spectroscopy with Electrons (ER-C), 52425 Jülich, Germany

<sup>2</sup> Forschungszentrum Jülich GmbH, Institute of Energy Materials and Devices, Materials Synthesis and Processing (IMD-2), 52425, Jülich, Germany

<sup>3</sup> University of Stuttgart, Institute for Manufacturing Technologies of Ceramic Components and Composites (IFKB), 70569, Stuttgart, Germany

<sup>4</sup> Forschungszentrum Jülich GmbH, Peter Gruenberg Institute for Electronic Materials (PGI-7), 52425 Jülich, Germany

<sup>5</sup> Instituto de Tecnología Química, Universitat Politècnica de València – Consejo Superior de Investigaciones Científicas, Av. Los Naranjos, s/n, 46022 Valencia, Spain

<sup>6</sup> MESA+ Institute for Nanotechnology, University of Twente, P. O. Box 217, Enschede, 7500AE, The Netherlands

<sup>7</sup> RWTH Aachen University, Central Facility for Electron Microscopy (GFE), 52074 Aachen, Germany

<sup>8</sup> Jülich Aachen Research Alliance, JARA-Energy, 52425, Jülich, Germany

#### Corresponding authors:

#### m.kindelmann@fz-juelich.de

o.guillon@fz-juelich.de

# Keywords:

Defect segregation, Grain boundaries, Protonic ceramics, Space charge

https://doi.org/10.26434/chemrxiv-2024-svz4w ORCID: https://orcid.org/0000-0001-9676-2090 Content not peer-reviewed by ChemRxiv. License: CC BY-NC-ND 4.0

# Abstract

Acceptor-doped barium zirconates are of major interest as proton-conducting ceramics for electrochemical applications at intermediate operating temperatures. The proton transport through polycrystalline microstructures of yttrium doped barium zirconates is hindered by the presence of a positive space charge potential at grain boundaries. During high temperature sintering, the positive charge acts as a driving force for acceptor dopant segregation to the grain boundary. Acceptor segregation to grain boundaries has been observed in sintered ceramics, but the fundamental relationship between the segregation kinetics and the protonic conductivity is poorly understood. Here, we present a comprehensive study of the influence of acceptor dopant segregation on the electrochemical properties of grain boundaries in barium zirconate based protonic ceramics. To facilitate this study, we designed an out-of-equilibrium model material that is not in a state of thermodynamic equilibrium and displays no detectable Y segregation at its grain boundaries. This model material served as a starting point to measure the kinetics of segregation and the induced changes in grain boundary conductivity upon varying thermal histories. Furthermore, we correlated the electrochemical results from impedance spectroscopy to atomic resolution transmission electron microscopy and atom probe tomography. We discovered that acceptor dopant segregation drastically increases the proton conductivity in both our model system and several other application-relevant compositions. In all cases, high-temperature thermal treatments were necessary to equilibrate the space charge zones, allowing the segregation of cationic point defects to grain boundaries, compensating the core charge and resulting in high performance protonic ceramics.

# Introduction

Solute segregation to grain boundaries greatly impacts the bulk properties of polycrystalline solids. This includes structural, chemical and functional properties, in metallic and ceramic materials <sup>1–4</sup>. Segregation phenomena are especially important for ceramic ionic and mixed electronic-ionic conductors, where grain boundaries can drastically decrease the ionic transport <sup>5–7</sup>. Ion-conducting ceramics are highly relevant for a wide variety of energy applications ranging from solid state batteries <sup>8,9</sup> to solid oxide fuel and electrolyser cells <sup>10–14</sup> and membrane reactors <sup>15–19</sup>, and are pivotal for future fossil-free energy systems. Recently, electrochemical devices based on proton-conducting ceramics have shown immense potential due to their reversible and robust performance in different operating modes<sup>20,21</sup>. Enabled by a dissociative hydration of water into oxygen vacancies (Equation 1), the transport of protons is made possible through a combination of reorientation and hopping, generally known as the Grotthuss mechanism <sup>22</sup>.

$$H_2 0 + V_0^{..} + O_0^{\chi} \to 20 H_0^{.}$$
 (1)

Most high-performance proton conducting oxides are based on a solid solution of the perovskites  $BaZrO_3$  and  $BaCeO_3$  using  $Y^{3+}$ ,  $Yb^{3+}$  or other trivalent dopants as acceptors  $^{10,22-24}$ . This material system allows the adjustment of the perovskite's stability and conduction properties to meet the operational requirements of specific applications like stability against steam and  $CO_2$  at elevated temperatures.

Barium zirconate-based proton conductors suffer from low grain boundary conductivities due to their positively charged interfaces, caused by oxygen vacancy segregation <sup>25–28</sup>. The accumulation of vacancies leads to the formation of a negatively charged space charge layer (SCL) adjacent to the interface, induced by the redistribution of point defects, hindering the transport of protons <sup>26,29–</sup>

<sup>31</sup>. During high-temperature thermal treatment, the positive core charge at grain boundaries acts as a driving force for the segregation of acceptor dopants to the interface, leading to their enrichment in the grain boundary core and/or the SCL <sup>29,32,33</sup>. The segregation of negatively charged point defects can partially compensate for the positive core charge, leading to an increase in grain boundary conductivity, for example, observed after high temperature thermal annealing of Y and Sc doped BaZrO<sub>3</sub> <sup>29,32,34</sup>. However, the kinetics of segregation have not been explored due to the lack of a non-equilibrated model system and most reports study segregation only phenomenologically using transmission electron microscopy (TEM)<sup>32,34–37</sup> or atom probe tomography (APT)<sup>33,38,39</sup>.

Until now, a fundamental relationship between the kinetics of acceptor dopant segregation and the resulting grain boundary conductivity is lacking. As the formation of acceptor dopant segregation is happening at elevated temperatures, where cationic diffusion is sufficiently high, all conventionally processed samples exhibit a grain boundary defect chemistry that is dependent on their specific thermal history (processing temperature, dwell time and cooling rate). The measured interfacial chemistry at room temperature is therefore dominated by two restricted equilibria <sup>40,41</sup>: 1) the acceptor dopant concentration is "frozen in" below a critical temperature, where cationic diffusion is extremely slow. 2) below that temperature oxygen vacancies ( $V_0^{\bullet\bullet}$ ) are still mobile, until the interface reaches a third temperature regime where all defects are immobile. So far, the unavoidable equilibration of the grain boundary defect chemistry during high temperature treatment has prevented a systematic investigation of the acceptor segregation kinetics and how this affects the transport properties of ion-conducting ceramics.

Here, we present a comprehensive study on the kinetics of acceptor dopant segregation and its impact on the electrochemical performance of BaZrO<sub>3</sub>-based proton conductors. Building on the

recently discovered, slow cation defect redistribution at grain boundaries in undoped SrTiO<sub>3</sub> during low temperature, high-pressure spark plasma sintering<sup>42</sup>, we developed a processing scheme that completely suppresses yttrium acceptor dopant segregation, and therefore allows us to investigate the extent and the kinetics that acceptor segregation poses on the grain boundary conductivity in BaZrO<sub>3</sub> based proton conductors. Targeted thermal treatments are used to systematically change the grain boundary properties through controlled acceptor segregation. We correlated the bulk electrochemical properties with the chemical composition and bonding environment at the grain boundary using atomically resolved characterization techniques to reveal that high proton conductivities are enabled by the atomically sharp segregation of yttrium acceptor dopants to the first atomic plane at the grain boundary. The continuous segregation of yttrium to the grain boundaries leads to decreased space charge potentials, enabling high protonic conductivities. Even though this study focuses on the characterization of the protonic ceramic  $BaZr_{0.7}Ce_{0.2}Y_{0.1}O_{3-\delta}$ , the phenomenon of segregation-controlled conductivity is demonstrated to be transferable to all highly relevant BaZrO<sub>3</sub> based compositions (including BaZr<sub>0.8</sub>Y<sub>0.2</sub>O<sub>3-δ</sub> (BZY20), BaZr<sub>0.5</sub>Ce<sub>0.3</sub>Y<sub>0.2</sub>O<sub>3-δ</sub> (BZCY532) and BaZr<sub>0.4</sub>Ce<sub>0.4</sub>Y<sub>0.1</sub>Yb<sub>0.1</sub>O<sub>3-δ</sub> (BZCYYb441)). Our results clearly illustrate the importance of high-temperature treatments beyond 1300 °C in equilibrating the defect chemistry at grain boundaries in proton-conducting ceramics, which is crucial to facilitate high proton conductivities. Additionally, the presented findings are highly relevant for other oxide-based ionic conductors and electroceramics, where understanding grain boundary segregation might open new possibilities for the design and improvement of material properties.

# Controlling conductivity through targeted interfacial equilibration

Fig. 1 compares the conductivity of  $BaZr_{0.7}Ce_{0.2}Y_{0.1}O_{3-\delta}$  (BZCY) ceramics with different thermal histories. To study the impact of various equilibration temperatures, we designed a starting

material that has not been equilibrated at high sintering temperatures such as conventionally processed BZCY. Therefore, pure BZCY powders were sintered to high relative densities using field assisted sintering/spark plasma sintering (FAST/SPS). This approach allows the use of high heating and cooling rates ( $\pm 150$  °C/min) and a very short dwell time (5 min) at comparably low temperatures (1450 °C) <sup>42,43</sup>. This processing procedure yields ultrafine, dense samples (Fig. 1b, top, grain size:  $350 \pm 175$  nm),



Figure 1: Influence of the thermal history on the grain boundary conductivity of BaZr<sub>0.7</sub>Ce<sub>0.2</sub>Y<sub>0.1</sub>O<sub>3.6</sub>. (a) Schematic representation of the thermal history for the different BZCY samples shown here. (cooling rates and dwell time are -150 K/min and 5 min for the SPS cycle and – 5K/min and 5 h for the furnace runs). (b) EBSD orientation mappings showing no changes in the microstructure of the SPS sample (top) and the +1600 °C sample (bottom). The scale bar is 2  $\mu$ m. (c) Nyquist plots from electrochemical impedance spectroscopy at 300 °C in wet Ar/H<sub>2</sub> of the SPS (top) and +1600°C sample (bottom). The impedance data for all samples was fitted using two R||CPE circuits to separate the bulk from the grain boundary response and derive the total (d), bulk (e) and effective grain boundary (f). All conductivity plots also include literature values from BZCY ceramics of the same composition <sup>37,44,45</sup> and a reference sample produced by solid state reactive sintering (SSRS with 0.5 wt% NiO) denoted as solid lines.

which have a non-equilibrated grain boundary defect chemistry (as shown later), making them an optimal starting point to investigate the relationship between thermal history, acceptor dopant segregation, and grain boundary conductivity. A variation of thermal treatments was applied to systematically change the grain boundary defect chemistry between 1000 and 1600 °C (the schematic in Fig. 1a displays the two-step annealing process). Electrochemical impedance spectroscopy (EIS) was used to measure the conductivity at temperatures between 600 and 150 °C in wet Ar/H<sub>2</sub>. As a separation of the bulk and grain boundary semicircle above 400 °C is not possible, values between 400 - 600 °C are not displayed here <sup>46</sup>. Therefore, bulk and grain boundary contributions can be compared for the full temperature range. Fig. 1 c shows two Nyquist plots obtained from EIS measurements at 300 °C in wet Ar/H<sub>2</sub> to highlight the direct changes induced by a thermal treatment at 1600°C in air. The total impedance is strongly decreased, driven by a massive reduction of the grain boundary contribution. At the same time, the bulk impedance stays in the same order of magnitude. The complete impedance data set, which displays the total, bulk and effective grain boundary conductivities, respectively, is summarized in Fig. 1d-f. The total conductivity continuously increases, depending on the extent of the thermal treatment (1d), and reaches values comparable to samples in literature with the same composition after conventional processing <sup>37,44,45</sup>. Furthermore, we compared our model system to samples processed by the industrially applied solid state reactive sintering method (SSRS) and could also find comparable conductivities. The continuous increase in total conductivity is controlled by the grain boundary conductivity, which shows a comparable behaviour (1f), while the bulk conductivity remains relatively constant (1e). This effect is independent from the microstructure, as BaZrO<sub>3</sub> based materials show a sluggish grain growth behaviour, when no sintering aids are added <sup>47</sup>. Microstructure imaging and quantitative analysis (Fig. 1b) show that the average grain

size after the highest thermal treatment (+1600 °C) is still at  $320 \pm 172$ nm, confirming that no measurable grain growth could be observed. This proves that changes in grain boundary composition and interfacial defect chemistry are most possibly responsible for the strong increase in protonic conductivity after equilibration of the samples at high temperatures, while a relative change in the interfacial area between grain boundaries can be excluded as the origin of the observed effect.



**Figure 2: Impact of segregation kinetics on space charge potential and protonic conductivity.** (a) Space charge potential after varied thermal histories calculated from EIS data using equation (2). (b) Schematic representation of the charge compensation mechanism induced by acceptor segregation during thermal annealing. (c) The effective grain boundary conductivity at 400 °C in wet Ar/H<sub>2</sub> derived from EIS measurements after different annealing treatments between 1000 and 1600 °C for 5 h to 30 h. (d) Processing map showing the total conductivity at 600 °C in Ar/H<sub>2</sub> after different equilibration treatments. The dashed line represents a conductivity of 1mS/cm.

If the segregation of acceptor dopants is the major factor driving the increase in grain boundary conductivity through charge compensation, this should also reduce the space charge potential  $\phi_0$ , which can be derived from EIS data using equation (2)<sup>48,49</sup>. More details about equation (2) can be found in the methods part.

$$\frac{\omega_{Bulk}}{\omega_{GB}} = \frac{e^{z_j F \phi_0/RT}}{2 \, z_j F \phi_0/RT} \qquad (2)$$

Fig. 2a displays the space charge potential  $\phi_0$  for samples after thermal treatments at temperatures between 1000 - 1600°C. The potential in samples annealed at lower temperatures is the highest, with values around 0.25 to 0.27 V. Nevertheless, it is still significantly lower than reported for BaZrO<sub>3</sub> based proton conductors (0.5 to 0.6 V at 250°C <sup>36,50</sup>), possibly due to high oxygen partial pressure (wet oxidizing atmosphere) used in the referenced studies. Thermal annealing at temperatures above 1300°C leads to a further significant decrease of the space charge potential down to values of 0.17 V. However, these values lie still above the space charge potential derived from reference samples processed by SSRS, most likely due to additional charge compensation mechanisms induced by the segregation of Ni to the grain boundary (also leading to a high effective GB conductivity observed in Fig. 1f)<sup>38,39</sup>. Since microstructural changes were not observed in our model samples, the compensation of the positive core charge at the grain boundary through acceptor dopant segregation is possibly the dominant mechanism enabling high grain boundary conductivity. The schematic in Fig. 2b explains the basic principle of this mechanism, in which the potential at an interface is significantly higher due to a homogeneous distribution of acceptor dopants across the interface. The thermally activated segregation of negatively charged  $Y'_{Zr}$  cations to the interface (driven by the core charge), then compensates for parts of the positive core charge, leading to a reduction of the space charge potential.

To further understand the kinetics of segregation, more extended annealing experiments were conducted at 1000, 1200, 1400 and 1600 °C in a range between 5 and 30 h in air and investigated by EIS. Fig. 2c shows the changes in the grain boundary conductivity after these treatments, starting from the non-equilibrated samples state (black circle). Large increases in conductivity can be observed after short annealing times. However, due to insufficient cation diffusion kinetics at temperatures below 1400 °C, a full equilibration could not be achieved for these samples. Since the positive core charge acts as the major driving force for yttrium segregation to the grain boundary, the process decelerates until a balance is reached between further segregation and the interfacial space charge potential.

Even though separation of bulk and grain boundary conductivities is not possible at temperatures above 600 °C, the systematic annealing treatments done here allow us to map out the interfacial equilibration times and temperatures, which are needed to surpass a minimum total conductivity of 1 mS/cm in wet Ar/H<sub>2</sub> (Fig. 2d). For the BZCY composition investigated here, temperatures above 1300 °C (and sufficiently long dwell times) enable the progressive grain boundary equilibration and thus, reaching the total conductivity magnitude needed for practical application.

## Observing acceptor segregation at the atomic scale

To understand the atomistic reasons for the continuous conductivity increase after thermal treatments at varied temperatures, we investigated grain boundaries in non-equilibrated (SPS) and thermally treated (SPS +1600 °C) samples using high resolution scanning transmission electron microscopy (STEM) and atom probe tomography (APT). Fig. 3 summarizes the characterization of the chemical composition and the structure at grain boundaries in both sample types. Fig. 3 a-b shows high angle angular dark field (HAADF) images and electron dispersive X-ray spectroscopy

(EDS) elemental mappings of general grain boundaries in the non-equilibrium state (a) and after high temperature treatment (b).



**Figure 3: Segregation behaviour at BZCY grain boundaries before and after high temperature equilibration.** High resolution STEM images and EDS mappings of general grain boundaries in SPS (a) and +1600 (b) showing the absence before, and the atomically sharp yttrium segregation after thermal annealing. The scale bar is 2 nm. Integrated line scans (highlighted in the corresponding Ba mapping) reveal the chemical composition at the interface of SPS (c) and +1600 BZCY (d) (dashed lines correspond to the grain boundary core). EELS spectra of the O K-edge (e) and the Ce M4,5-edge (f) derived from the bulk and the grain boundary core. (g) APT elemental map of the +1600 BZCY sample showing Ce atoms and an Y isoconcentration surface (3.6 at%) decorating grain boundaries. The data set contains five grain boundaries and a triple junction. (i) a concentration profile of the major elements across the grain boundary indicated in (g).

The yttrium distribution at the interface is drastically changing from being homogeneous across the interface, to a strong segregation to the first B-site plane at the grain boundary. The differences are additionally highlighted by integrated line scans across the grain boundaries and along the [110] planes of the oriented grain on the right (Fig. 2 c-d). After high-temperature treatment, yttrium cations strongly segregate to the first B-site plane of the perovskite lattice and the grain boundary core, substituting large amounts of zirconium cations, thereby compensating the positive core charge <sup>29</sup>.

In addition to an elastic driving force induced by cationic size mismatch <sup>51,52</sup>, the segregation is driven by the space charge potential at the grain boundary, generated by oxygen vacancy accumulation <sup>26,28</sup>. This leads to high local yttrium concentrations of around 8 at% (estimated from EDS by a standard-less quantification) on the last B-site plane. This correlates to 43 at% of yttrium on the B-site, which is far above the solubility limit for yttrium in BaZrO<sub>3</sub>.based perovskites <sup>53</sup>. The high local concentration of yttrium (which acts as a negative point defect, i.e.  $Y'_{Zr}$ ) can partially compensate the positive core charge, decreasing the space charge potential and thereby lowering the barrier for proton conduction across the grain boundaries. This results in the strong increase in grain boundary conductivity (Fig. 1 f) and a decrease of the space charge potential (Fig. 2 a), measured using EIS.

Additionally, electron energy loss spectroscopy (EELS, Fig. 2 e-f) helps to understand the influence of segregation on the local oxygen bonding environment and the Ce valency at the grain boundary. Both graphs show integrated spectra of the same size (1 nm x 3 nm) taken from the grain boundary core and an adjacent "bulk" region (details on the EELS analysis can be found in Fig. S2). Non-equilibrium grain boundaries show a clear reduction in the intensity of the oxygen K edge and significant changes in the fine structure, induced by the depletion of oxygen in the

grain boundary core <sup>54</sup>. However, the corresponding Ce  $M_{4,5}$  edge does not reveal differences between bulk and grain boundary. After thermal annealing at 1600°C clear changes in both the oxygen K and the Ce  $M_{4,5}$  edge are visible (red spectra). Both intensity and fine structure of the oxygen K edge at the grain boundary are approaching the characteristics, which can be observed in the bulk. In contrast to the O K edge, the intensity of the Ce  $M_{4,5}$  edge after thermal treatment decreases in intensity at the grain boundary, most likely due to a substitution of Ce<sup>4+</sup> by Y<sup>3+</sup> cations. Comparing the ratio of the intensities of the Ce  $M_5$  to the  $M_4$  edge, which can be used to assess the valence state of Ce <sup>6,55</sup>, did not reveal significant changes between bulk and grain boundary, before and after equilibration of the grain boundaries (0.74 to 0.73 for the SPS sample and 0.72 to 0.71 for the +1600 sample from bulk and GB measurements, respectively). Additionally, XPS measurements on bulk samples revealed no significant changes in the core-level signatures and in the relative composition of the sample in the non-equilibrium and equilibrium state, highlighting that changes in defect chemistry and electronic signature are truly localized to the grain boundary region, which is undetectable by XPS (details on the XPS analysis can be found in Fig. S3).

The gained insights on yttrium segregation from HR-STEM were also confirmed by electrostatic analysis and density functional theory (DFT) computing the segregation energy for Y and Yb cations that diffuse from bulk to GB lattice sites (details on the atomistic models and computational setup can be found in Fig. S4 and the method section). The segregation energies in a representative GB model simulating a symmetric  $\Sigma 3$  [110]/(-112) tilt GB for Y and Yb cations are calculated as -0.89 and -1.00 eV/atom, respectively. The segregation energies for Y and Yb are much larger than that calculated by A. Lindmann et al.<sup>28</sup> for Y without having oxygen vacancy at the GB (-0.32 eV). This is because the clustering of oxygen vacancies with Y<sup>3+</sup>/Yb<sup>3+</sup> cations is electrostatically more favourable than that with  $Zr^{4+}$ . This result shows that oxygen vacancies clearly increase the driving force for Y/Yb segregation at elevated temperatures.

As the chemical resolution of transmission electron microscopy techniques is insufficient to derive exact concentrations on the local defect chemistry, atom probe tomography (APT) was applied to assess the composition of grain boundaries after thermal annealing. Fig. 3 g-i shows the 3D reconstruction of an APT dataset, which includes five grain boundaries and a triple junction, as well as a concentration profile built across one of the grain boundaries. The high mass resolution and quantitative nature of APT allow for calculating of the Gibbsian interfacial excess  $\Gamma_i$ , giving exact values for the segregation of yttrium and minor impurities (strontium and calcium) to the grain boundary (see supplementary Tab.S1). An approximation of the Langmuir – McLean description for solute segregation, makes an estimation of the average diffusion coefficient D<sub>Y</sub> of Y to the grain boundaries in BZCY possible using equation (3) <sup>56</sup>. Details on the calculation can be found in the methods section.

$$\frac{X_b(t) - X_b(0)}{X_b(\infty) - X_b(0)} = \frac{2}{\beta} \frac{b^2}{a^3} \left(\frac{4Dt}{\pi}\right)^{1/2}$$
(3)

For the segregation of yttrium from a completely non-equilibrated state to an average grain boundary excess of  $\Gamma_Y = 6.3$  at/nm<sup>2</sup>, a diffusion coefficient  $D_Y = 0.25 \times 10^{-24} m^2/s$  can be estimated. Compared to the bulk diffusion coefficients of cations in other perovskite oxides like BaTiO<sub>3</sub> and SrTiO<sub>3</sub>,  $D_Y$  is comparably low <sup>57–59</sup>, which agrees well with the general refractive nature of this material, requiring high sintering temperatures (>1500°C for BZCY compared to e.g. 1150°C for BaTiO<sub>3</sub>). However, the driving force assumption for equation (3) may not be complete as it ignores electrostatic contributions, and the presented value should be considered as an estimation. Note that this is a general issue of diffusion coefficients, particularly for grain boundary processes, and this study is one of the rare cases where an approximation is possible at all.

Furthermore, combining the high spatial resolution of STEM/EDS and the chemical resolution of APT enables us to calculate the atomic percentage of acceptor dopants on the last B-site plane at the grain boundary, giving an insight into the local chemistry. As the planar density of the B-site in Y-doped BaZrO<sub>3</sub> in the [100] plane is 6.25 at/nm<sup>2</sup>, and the average yttrium excess at the grain boundary is 6.3 at/nm<sup>2</sup> (distributed across both B-site planes at the GB and the GB core, see Fig. 3d), all three atomic positions have an average 43.6 at% yttrium occupancy. Considering a bulk solubility of yttrium on the B-site of roughly 30 at% <sup>60,61</sup> the grain boundary composition we measured both in STEM-EDS and APT clearly surpasses these values and reveals a complexion-like thermodynamically stable grain boundary phase <sup>62</sup>.

However, the analysis of various GBs using APT also revealed deviations in interfacial acceptor dopant excess, varying between 4.9 and 7.9 at/nm<sup>2</sup> (see Tab. S1). This shows the strong influence the grain boundary character has on the segregation behaviour, highlighting the need for further correlative microscopy and modelling approaches to reveal the fundamental relationships between segregation, grain boundary properties and the related transport mechanisms  $^{63,64}$ .

## Segregation controlled conductivity in other relevant proton conducting ceramics

Fig. 4 compares the conductivity of the most important proton-conducting ceramics based on BaZrO<sub>3</sub>. In addition to BaZr<sub>0.7</sub>Ce<sub>0.2</sub>Y<sub>0.1</sub>O<sub>3- $\delta$ </sub> (BZCY721, 4b), we investigated compositions without cerium BaZr<sub>0.8</sub>Y<sub>0.2</sub>O<sub>3- $\delta$ </sub> (BZY20, 4a), with higher cerium contents BaZr<sub>0.5</sub>Ce<sub>0.3</sub>Y<sub>0.2</sub>O<sub>3- $\delta$ </sub> (BZCY532, 4c) and a co-doped composition with high cerium content BaZr<sub>0.4</sub>Ce<sub>0.4</sub>Y<sub>0.1</sub>Yb<sub>0.1</sub>O<sub>3- $\delta$ </sub> (BZCYYb4411, 4d). All materials were sintered by FAST/SPS at low temperatures and short dwell

times under mechanical pressure, to bring them into a densified and non-equilibrated state and afterwards annealed for 5 h at 1600 °C. For both sample states, the total and the effective grain boundary conductivity are displayed, to showcase the impact a high-temperature equilibration of the grain boundary defect chemistry has on the performance of different ceramic proton conductors.



**Figure 4: Segregation-controlled conductivity changes in different scientifically important BaZrO<sub>3</sub> based proton conductors.** Electrochemical impedance spectroscopy in wet Ar/H<sub>2</sub> of BaZr<sub>0.8</sub>Y<sub>0.2</sub>O<sub>3-6</sub> (BZY20) (a), BaZr<sub>0.7</sub>Ce<sub>0.2</sub>Y<sub>0.1</sub>O<sub>3-6</sub> (BZCY721) (b), BaZr<sub>0.5</sub>Ce<sub>0.3</sub>Y<sub>0.2</sub>O<sub>3-6</sub> (BZCY532) (c) and BaZr<sub>0.4</sub>Ce<sub>0.4</sub>Y<sub>0.1</sub>Yb<sub>0.1</sub>O<sub>3-6</sub> (BZCYYB4411) (d) samples after SPS and post thermally treated for 5 h at 1600 °C in air. Total and effective grain boundary conductivity are represented by squares and triangles, respectively. Literature data in all plots is visualized by lines <sup>13,37,44,45,65–68</sup>.

All compositions show a strong increase in total conductivity after the thermal treatment, mainly caused by the increase in effective grain boundary conductivity. The cerium content on the B-site of the perovskite has a positive effect on the performance in the non-equilibrated state, which is highest for compositions with a higher cerium content. The cerium-free composition (BZY20) shows the worst electrochemical performance in the non-equilibrium state, making it complicated to separate bulk and grain boundary contributions (details on the fitting of the electrochemical data can be found in Fig. S5), due to the dominating impact of grain boundaries. Therefore, only the total conductivity can be derived from these measurements.

The increased diffusion coefficients for cations in BaZrO<sub>3</sub> – BaCeO<sub>3</sub> solid solutions are leading to coarser microstructures (details on the microstructure can be found in Fig. S6) and might be one explanation for the continuous increase in conductivity in the non-equilibrated samples from BZY20 to BZCYYb4411. The higher interdiffusion clearly complicates the conservation of a non-equilibrium grain boundary defect chemistry during FAST/SPS <sup>59</sup>. Comparing our measurements to literature data, it becomes evident that the performance of conventionally processed protonic ceramics is reached after an equilibration of the grain boundary defect chemistry. Minor deviations can be observed only for several studies that used high temperature sintering (1600 °C) and extensive dwell times (24 h) to sinter BZY20 <sup>65,66</sup> and BZCYYb4411 <sup>13</sup>. These processing parameters exceed the thermal treatment applied here, leading to larger grain sizes and consequently a lower overall grain boundary resistance.

Our study reveals the fundamental importance of sufficiently high thermal treatments (either during sintering or by a post-thermal treatment) to enable acceptor dopant segregation to the grain boundary, compensating the positive core charge and lowering the intrinsic space charge potential. This behaviour is responsible for the high protonic conductivity in all currently applied protonic

ceramics, based on acceptor-doped BaZrO<sub>3</sub>. Furthermore, the understanding of the relationship between thermal history and grain boundary defect chemistry can be a novel design parameter to optimize the properties of various electroceramics by tuning their grain boundary segregation.

# Conclusions

In this study, we developed model materials based on the ceramic proton conductor BaZr<sub>0.7</sub>Ce<sub>0.2</sub>Y<sub>0.1</sub>O<sub>3- $\delta$ </sub>, suitable for investigating the kinetics of solute segregation to grain boundaries and its influence on protonic conductivity. Through the systematic variation of thermal treatments between 1000 and 1600 °C, we were able to continuously increase the grain boundary conductivity by altering its defect chemistry from a non-equilibrium to an equilibrated state, without significant changes in the grain size. The drastic increase in protonic conductivity could be directly associated with the atomically sharp segregation of the yttrium acceptor dopant to the grain boundary after high-temperature treatment. The presence of negatively charged  $Y'_{Zr}$  point defects directly adjacent and in the grain boundary core compensates part of the intrinsic positive core charge, subsequently lowering the overall space charge potential and facilitating proton transport across grain boundaries.

The combination of high spatial resolution spectroscopy in STEM and the high 3D elemental sensitivity of APT allowed us to determine the local chemistry of non-equilibrium as well as equilibrated grain boundaries. This enabled us to derive the fundamental relationships between the measured protonic conductivity, the chemistry at grain boundaries, and the space charge potential while excluding the influence of sintering aids and varying microstructures. Our results highlight the importance of sufficiently high thermal treatments above 1300 °C, to facilitate acceptor dopant segregation and enable high protonic conductivities in this class of materials.

We could additionally show that this behaviour can be observed in most commonly applied compositions of ceramic proton conductors based on BaZrO<sub>3</sub>, independently of the B-site composition. Therefore, the fundamental insights reported here are applicable to a broad variety of materials used in solid oxide fuel and electrolysis cells, as well as membrane reactors. Even though the influence of acceptor dopant segregation has been exemplified for ceramic proton conductors here, the understanding of this behaviour is highly relevant for a wide variety of functional ceramics, where control over grain boundary properties is essential in harnessing their optimal performance.

# Methods

# Starting powders and sintering

In this study, commercial powders of the nominal composition BaZr<sub>0.7</sub>Ce<sub>0.2</sub>Y<sub>0.1</sub>O<sub>3-δ</sub> (BZCY721), BaZr0.5Ce0.3Y0.2O3-8 (BZCY532) and BaZr0.4Ce0.4Y0.1Yb0.1O3-8 (BZCYYb4411, all Marion Technologies, well self-synthesized BaZr<sub>0.8</sub>Y<sub>0.2</sub>O<sub>3-δ</sub> France) as as (BZY20) and BaZr<sub>0.7</sub>Ce<sub>0.2</sub>Y<sub>0.1</sub>O<sub>3-δ</sub> (0.5 wt% NiO, SSRS-BZCY721) powders have been applied. Details on the mixed oxide powder synthesis route can be found elsewhere <sup>35,47,69</sup>. All powders are sintered using a field assisted sintering / spark plasma sintering (FAST/SPS) device (HP-D5, FCT Systeme, Germany). Compositions with a low amount of Ce were densified at 1450 °C for 5 min with 80 MPa of uniaxial pressure applied, while Ce-rich compositions (BZCY532 and BZYYb4411) were sintered at 1350 °C for 5 min using a uniaxial pressure of 50 MPa. The heating and cooling rates for both experiments were 150 K/min, enabling fast densification and the preservation of a nonequilibrium grain boundary defect chemistry. All thermal treatments are done in air furnaces

between 1000 and 1600 °C from 5 to 30 h. To prevent Ba evaporation at higher temperatures, thermal treatments above 1400 °C were conducted in sacrificial powder of the same composition.

#### Electrochemical impedance spectroscopy

Electrochemical impedance spectroscopy (EIS) was used to assess the proton conductivity of all samples investigated in the scope of this study. To separate bulk and grain boundary contributions, the impedance was measured in the range between 600 and 150 °C using an Alpha-A High Performance Frequency Analyzer, (Novocontrol, Germany) in the frequency range of 10 MHz to 0.1 Hz in wet Ar/2.9%H<sub>2</sub> (p(H<sub>2</sub>O) ~0.025 bar). The impedance data was fitted using a series of equivalent circuits consisting of parallels of a resistance and constant phase element (R||CPE) and interpreted using the brick layer model<sup>46</sup> in RelaxIS3 (rhd instruments, Germany). The R||CPE elements were attributed to bulk, grain boundary or electrode by calculating the specific capacitance<sup>46,70</sup>. Subsequently, the total, bulk and effective grain boundary conductivity are calculated using equations (1-3), respectively. In the given equations R<sub>b</sub> and R<sub>gb</sub> are the resistivities derived from the fitting and *l* and *A* are the thickness and area of the measured sample.

$$\sigma_t = \frac{1}{(R_b + R_{gb})} \frac{l}{A} \tag{4}$$

$$\sigma_b = \frac{1}{R_b} \frac{l}{A} \tag{5}$$

$$\sigma_{eff.gb} = \frac{1}{R_{ab}} \frac{l}{A} \tag{6}$$

## Scanning transmission electron microscopy

Samples for scanning transmission electron microscopy (STEM) were prepared using a conventional dimpling route to achieve a large area of electron transparent materials, facilitating the search for suitable grain boundaries for high resolution analysis. Bulk samples were first metallographically ground and polished to a thickness of 100  $\mu$ m and afterwards dimple grinded to a minimal thickness of 10 to 15  $\mu$ m using a dimple grinder (Gatan Inc., USA). Afterwards the final hole was milled and thinned using an Ar ion milling device (PIPS II, Gatan Inc., USA). High resolution STEM imaging and spectroscopy was done using a probe C<sub>s</sub>-corrected Spectra 300 microscope (Thermo Fischer Scientific, USA) at 200 keV. The microscope is equipped with a Super-X EDS detector and a Gatan Continuum 1066 energy filter (GIF). Data analysis of the EDS results was done using the Velox software (Thermo Fischer Scientific, USA). Quantification of the EDS measurements was done using a standard less (Cliff-Lorimer) method to estimate the composition at the grain boundary. High errors are assumed as the quantification does not consider absorption and channelling. The analysis of the EELS data was done using the Python package HyperSpy.

# Atom probe tomography

APT specimens were prepared from the polished sample surface by the conventional lift-out technique using a dual-beam focused-ion-beam (FIB) system (FEI Helios Nanolab 600i). To reduce Ga implantation in the APT-ready sample, 2 keV Ga beam was used for final cleaning of specimens. APT analyses were performed using a reflectron-equipped local electrode atom probe tool (LEAP 4000X HR, Cameca Instruments, USA) in laser mode. Laser pulses of 355 nm wavelength, 12 ps pulse length, 10-20 pJ pulse energy and 200 kHz frequency were applied. The specimen base temperature was kept at about 25 K and the detection rate was maintained at 0.005 or 0.01 ion per pulse. Data reconstruction and analysis was performed using Cameca IVAS 3.6.14

software package. Reconstruction parameters were derived from comparing the pre- and postanalysis SEM images of APT specimens, so that correct dimensions of the reconstructed dataset (final specimen radius and the length of the field-evaporated volume) are ensured. Three APT datasets, each containing 2 to 5 grain boundaries, were analysed in total.

# **Density functional theory calculations**

Grain boundary (GB) models were constructed by using Aimsgb<sup>71</sup> employing 48 formula units of BZO, containing two identical grain boundaries, due to periodic boundary conditions. We first started to find the most favourable sites for two oxygen vacancies and four Y/Yb ions in a GB  $\Sigma_{3}[110]/(-112)$  grain boundary (GB) by performing Coulomb energy calculations on 2003395680  $(2.0 \times 109)$  possible combinations/permutations employing the Supercell code <sup>72</sup>. We used charges of 2+ for Ba, 4+ for Zr, 3+ for Y/Yb and 2- for oxygen. To model the SPS-sintered GB, a similar approach was utilized. To accommodate Y/Yb ions in the bulk region of our GB model, we artificially introduced two fixed trivalent ions next to the optimal oxygen vacancy position at the GB to repel four Y/Yb ions from the GB plane. To maintain the charge neutrality for this case, we reduced the Zr valence to +3.952 in this step. Subsequently, the artificially added trivalent ions at the GB plane were replaced by Zr ions. The resulting models are depicted in Fig. S4. To calculate the segregation energy, which is the total energy difference between Y/Yb at the GB plane and bulk region  $(E_{Y/Yb}(GB)-E_{Y/Yb}(Bulk))$ , we performed spin-polarized DFT <sup>73,74</sup> calculations as implemented in the Vienna Ab initio Simulation Package (VASP) code <sup>75</sup> using the PBE functional <sup>76</sup> and the Projector Augmented-Wave (PAW) method <sup>77</sup>. A  $\Gamma$ -point centred k-point mesh of 2×1×4 and energy cut-off of 520 eV as well as energy and force convergence criteria of  $5.0 \times 10^{-5}$  eV and 1.0×10<sup>-2</sup> eV/Å, respectively, were applied. Ionic positions and unit cell volume were fully optimized while the unit cell shape was fixed (ISIF=8). Pseudopotentials with valence electron configurations  $5s^2 5p^6 5d^{0.01} 6s^{1.99}$ ,  $2s^2 2p^4$ ,  $4s^2 4p^6 4d^3 5s^1$ ,  $4s^2 4p^6 4d^2 5s^1$ ,  $5p^6 5d^1 6s^2$  for Ba, O, Zr, Y and Yb were used, respectively.

## Calculation of space charge potential and Y diffusion coefficients

Space charge potentials were evaluated using equation (2) which is the solution of an 1D Poisson equation of a Schottky depletion layer<sup>48</sup>. In equation (2) R is the Boltzmann constant, F the Faraday constant,  $\Phi_0$  the space charge potential,  $z_j$  the valency of the mobile charge carrier ( $z_j = 1$  for Protons), *e* the elementary charge, T the temperature in K during EIS and,  $\omega_{Bulk}$  and  $\omega_{GB}$  are the relaxation frequencies of the bulk's and GBs' impedance signal. Either the ratio of the bulk's and grain boundaries' resistivity, capacitance, relaxation frequency or relaxation times can be used for space charge potential calculations. Either of these parameters are obtained from fitting impedance data with the aforementioned equivalent circuit. Relaxation frequencies were calculated using equation (7), where  $R_i$  and  $C_i$  are the total resistance and capacitance of the bulk or GB. Using the relaxation times or frequency give the best agreement with the true space charge potential at the GBs because these parameters are microstructure independent<sup>78</sup>.

$$\omega_i = \frac{1}{2\pi \cdot R_i C_i} \tag{7}$$

The diffusion coefficient for Yttrium segregation to grain boundaries was estimated using a Langmuir – McLean based model, where the segregation kinetics can be described by equation (8)  $^{56}$ ,

$$\frac{X_b(t) - X_b(0)}{X_b(\infty) - X_b(0)} = 1 - \exp\left(\frac{4Dt}{\beta^2 f^2}\right) \, erfc \, \left(\frac{4Dt}{\beta^2 f^2}\right)^{1/2} \tag{8}$$

Where  $X_b(t)$  is the concentration at the interface at different times, f is a ratio between the atomic sizes  $f = a^3 b^{-2}$  with a for the matrix and b for the solute. And  $\beta$  is the ratio between the concentration at the grain boundary to the concentration at the bulk,  $\beta = X_b/X_c$ .

For short dwell times below a full equilibration, this equation can be approximated by <sup>56</sup>:

$$\frac{X_b(t) - X_b(0)}{X_b(\infty) - X_b(0)} = \frac{2}{\beta} \frac{b^2}{a^3} \left(\frac{4Dt}{\pi}\right)^{1/2}$$
(9)

In the above applied estimation, we used the cationic size ratios of Y and Zr/Ce for b and a, as well as the atomic concentrations of Y on the B-site from APT measurements ( $X_b(t) = 44.3$  at% and  $X_b(0) = 20.0$  at%). The thermodynamic maximum of segregation was estimated to be 50 at%.

# Photoelectron X-ray spectroscopy

XPS (Phi 5000 VersaProbe, ULVAC Phi, Physical Electronics Inc.) was performed for the nonequilibrium and equilibrium sample state using the Al K $\alpha$ 1 line (E $\lambda$  = 1486.6 eV) of a monochromized X-ray source. Survey spectra and O 1s, C 1s, Si 2p, Ce 3d, Ba 3d, Zr 3d, Y 3d core-level spectra were obtained at a photoemission angle of  $\theta$  = 15°. Survey measurements were performed using a pass energy of E<sub>0</sub> = 187.85 eV. For the analysis of core-level spectra the pass energy was kept constant at E<sub>0</sub> = 23.5 eV for high energy resolution in the fixed analyser transmission mode.

All spectra were aligned with respect to the C 1s core-level signal BE = 284.8 eV. The survey spectra were normalized to the background signal between  $\Delta BE = 60-70$  eV. Core-level spectra were normalized to the pre-peak region ( $\Delta BE(O \ 1s)= 520-524$  eV,  $\Delta BE(Ce \ 3d)= 873-876$  eV,  $\Delta BE(Ba \ 3d)= 770-774$  eV,  $\Delta BE(Zr \ 3d)= 172-174$  eV,  $\Delta BE(Y \ 3d)= 147-149$  eV). No background

subtraction is applied. An offset is used along the y-axis to display the spectra in order to improve clarity. KolXPD version 1.8.0 was used for the evaluation of the data.

# Acknowledgement

Dr. Egbert Wessel (IMD-1, Forschungszentrum Jülich GmbH) is acknowledged for EBSD measurements. M.K is acknowledging the financial support from the DFG in the project MA 1280/69-1. J. E., D.J., M.P.Z. and W.R thank the DFG for funding within the Emmy Noether program (RH 146/1-1). J. M.S., S.E. and L.A. are acknowledging financial support by the Spanish Ministry of Science and Innovation (PID2022-139663OB-100 and CEX2021-001230-S grants funded by MCIN/AEI/10.13039/501100011033). P. K. and S. K. are acknowledging computing time granted through JARA-HPC on the supercomputer JURECA at Forschungszentrum Jülich under grant No. jiek12 and funding from the European Union under grant agreement No. 101099717 – ECOLEFINS project.

# References

- 1. Nie, J. F., Zhu, Y. M., Liu, J. Z. & Fang, X. Y. Periodic Segregation of Solute Atoms in Fully Coherent Twin Boundaries. *Science (80-. ).* **340**, 957–960 (2013).
- Buban, J. P. *et al.* Grain Boundary Strengthening in Alumina by Rare Earth Impurities. *Science* (80-.). **311**, 212–215 (2006).
- 3. Zhao, H. *et al.* How solute atoms control aqueous corrosion of Al-alloys. *Nat. Commun.* **15**, 1–9 (2024).
- 4. Lee, W. *et al.* Oxygen surface exchange at grain boundaries of oxide ion conductors. *Adv. Funct. Mater.* **22**, 965–971 (2012).
- 5. Guo, X. & Waser, R. Electrical properties of the grain boundaries of oxygen ion conductors: Acceptor-doped zirconia and ceria. *Prog. Mater. Sci.* **51**, 151–210 (2006).
- 6. Bowman, W. J., Zhu, J., Sharma, R. & Crozier, P. A. Electrical conductivity and grain boundary composition of Gd-doped and Gd/Pr co-doped ceria. *Solid State Ionics* **272**, 9–17 (2015).
- 7. Avila-Paredes, H. J. & Kim, S. The effect of segregated transition metal ions on the grain

boundary resistivity of gadolinium doped ceria: Alteration of the space charge potential. *Solid State Ionics* **177**, 3075–3080 (2006).

- 8. Janek, J. & Zeier, W. G. A solid future for battery development. *Nat. Energy* **1**, 1–4 (2016).
- 9. Schmaltz, T. et al. A Roadmap for Solid-State Batteries. Adv. Energy Mater. 13, (2023).
- 10. Yang, L. *et al.* Enhanced Sulfur and Coking Tolerance of a Mixed Ion Conductor for SOFCs: BaZr<sub>0.1</sub>Ce<sub>0.7</sub>Y<sub>0.2-x</sub>Yb<sub>x</sub>O<sub>3-d</sub>. *Science* (80-. ). **326**, 126–129 (2009).
- 11. Vøllestad, E. *et al.* Mixed proton and electron conducting double perovskite anodes for stable and efficient tubular proton ceramic electrolysers. *Nat. Mater.* **18**, 752–759 (2019).
- 12. Duan, C. *et al.* Highly durable, coking and sulfur tolerant, fuel-flexible protonic ceramic fuel cells. *Nature* **557**, 217–222 (2018).
- 13. Choi, S. *et al.* Exceptional power density and stability at intermediate temperatures in protonic ceramic fuel cells. *Nat. Energy* **3**, 202–210 (2018).
- Hauch, A. *et al.* Recent advances in solid oxide cell technology for electrolysis. *Science* (80-. ).
  370, (2020).
- 15. Deibert, W., Ivanova, M. E., Baumann, S., Guillon, O. & Meulenberg, W. A. Ion-conducting ceramic membrane reactors for high-temperature applications. *J. Memb. Sci.* **543**, 79–97 (2017).
- 16. Kyriakou, V. *et al.* Methane steam reforming at low temperatures in a BaZr<sub>0.7</sub>Ce<sub>0.2</sub>Y<sub>0.1</sub>O<sub>2.9</sub> proton conducting membrane reactor. *Appl. Catal. B Environ.* **186**, 1–9 (2016).
- 17. Malerød-Fjeld, H. *et al.* Thermo-electrochemical production of compressed hydrogen from methane with near-zero energy loss. *Nat. Energy* **2**, 923–931 (2017).
- 18. Daniel, C. *et al.* Single-step hydrogen production from NH<sub>3</sub>, CH<sub>4</sub>, and biogas in stacked proton ceramic reactors. *Science* (80-. ). **376**, 390–393 (2022).
- 19. Ding, D. *et al.* A novel low-thermal-budget approach for the co-production of ethylene and hydrogen via the electrochemical non-oxidative deprotonation of ethane. *Energy Environ. Sci.* **11**, 1710–1716 (2018).
- 20. Serra, J. M. Electrifying chemistry with protonic cells. *Nat. Energy* **4**, 178–179 (2019).
- 21. Duan, C., Huang, J., Sullivan, N. & O'Hayre, R. Proton-conducting oxides for energy conversion and storage. *Appl. Phys. Rev.* 7, (2020).
- 22. Kreuer, K. D. Proton-Conducting Oxides. Annu. Rev. Mater. Res. 33, 333–359 (2003).
- 23. Ryu, K. H. & Haile, S. M. Chemical stability and proton conductivity of doped BaCeO<sub>3</sub>–BaZrO<sub>3</sub> solid solutions. *Solid State Ionics* **125**, 355–367 (1999).
- 24. Katahira, K., Kohchi, Y., Shimura, T. & Iwahara, H. Protonic conduction in Zr-substituted BaCeO<sub>3</sub>. *Solid State Ionics* **138**, 91–98 (2000).
- 25. De Souza, R. A. The formation of equilibrium space-charge zones at grain boundaries in the perovskite oxide SrTiO<sub>3</sub>. *Phys. Chem. Chem. Phys.* **11**, 9939–9969 (2009).
- 26. De Souza, R. A., Munir, Z. A., Kim, S. & Martin, M. Defect chemistry of grain boundaries in

proton-conducting solid oxides. Solid State Ionics 196, 1-8 (2011).

- 27. Helgee, E. E., Lindman, A. & Wahnström, G. Origin of space charge in grain boundaries of proton-conducting BaZrO<sub>3</sub>. *Fuel Cells* **13**, 19–28 (2013).
- 28. Lindman, A., Bjørheim, T. S. & Wahnström, G. Defect segregation to grain boundaries in BaZrO<sub>3</sub> from first-principles free energy calculations. *J. Mater. Chem. A* **5**, 13421–13429 (2017).
- 29. Shirpour, M. *et al.* Dopant segregation and space charge effects in proton-conducting BaZrO<sub>3</sub> perovskites. *J. Phys. Chem. C* **116**, 2453–2461 (2012).
- 30. Shirpour, M., Merkle, R. & Maier, J. Evidence for space charge effects in Y-doped BaZrO<sub>3</sub> from reduction experiments. *Solid State Ionics* **216**, 1–5 (2012).
- Shirpour, M., Merkle, R., Lin, C. T. & Maier, J. Nonlinear electrical grain boundary properties in proton conducting Y-BaZrO<sub>3</sub> supporting the space charge depletion model. *Phys. Chem. Chem. Phys.* 14, 730–740 (2012).
- 32. Shirpour, M., Gregori, G., Houben, L., Merkle, R. & Maier, J. High spatially resolved cation concentration profile at the grain boundaries of Sc-doped BaZrO<sub>3</sub>. *Solid State Ionics* **262**, 860–864 (2014).
- 33. Clark, D. R. *et al.* Probing Grain-Boundary Chemistry and Electronic Structure in Proton-Conducting Oxides by Atom Probe Tomography. *Nano Lett.* **16**, 6924–6930 (2016).
- 34. Shirpour, M., Merkle, R. & Maier, J. Space charge depletion in grain boundaries of BaZrO<sub>3</sub> proton conductors. *Solid State Ionics* **225**, 304–307 (2012).
- Kindelmann, M. *et al.* Cold sintering of BaZr<sub>0.8</sub>Y<sub>0.2</sub>O<sub>3-δ</sub> ceramics: Phase formation and grain boundary properties. *J. Eur. Ceram. Soc.* (2023) doi:https://doi.org/10.1016/j.jeurceramsoc.2023.12.060.
- 36. Kjølseth, C. *et al.* Space-charge theory applied to the grain boundary impedance of proton conducting BaZr<sub>0.9</sub>Y<sub>0.1</sub>O<sub>3-δ</sub>. *Solid State Ionics* **181**, 268–275 (2010).
- 37. Huang, Y. *et al.* Effect of Ni on electrical properties of Ba(Zr,Ce,Y)O<sub>3-δ</sub> as electrolyte for protonic ceramic fuel cells. *Solid State Ionics* **390**, 116113 (2023).
- 38. Clark, D. R. *et al.* Understanding the effects of fabrication process on BaZr<sub>0.9</sub>Y<sub>0.1</sub>O<sub>3- $\delta$ </sub> grainboundary chemistry using atom probe tomography. *J. Mater. Chem. C* **11**, 5082–5091 (2023).
- 39. Kindelmann, M. *et al.* Highly conductive grain boundaries in cold-sintered barium zirconate-based proton conductors. *J. Mater. Chem. A* **12**, 3977–3988 (2024).
- 40. Usler, A. L. & De Souza, R. A. A Critical Examination of the Mott–Schottky Model of Grain-Boundary Space-Charge Layers in Oxide-Ion Conductors. *J. Electrochem. Soc.* **168**, 056504 (2021).
- 41. Usler, A. L., Ketter, F. & De Souza, R. A. How space-charge behaviour at grain boundaries in electroceramic oxides is modified by two restricted equilibria. *Phys. Chem. Chem. Phys.* (2024) doi:10.1039/D3CP05870K.
- 42. Zahler, M. P., Jennings, D., Kindelmann, M., Guillon, O. & Rheinheimer, W. Reactive FAST/SPS sintering of strontium titanate as a tool for grain boundary engineering. *J. Eur. Ceram. Soc.* (2023)

doi:10.1016/j.jeurceramsoc.2023.07.021.

- Wallis, J., Ricote, S., Weltmann, K. D., Burkel, E. & Kruth, A. The influence of the sintering temperature on BaZr<sub>0.7</sub>Ce<sub>0.2</sub>Y<sub>0.1</sub>O<sub>3-δ</sub> proton conductors prepared by Spark Plasma Sintering. *Ceram. Int.* 47, 15349–15356 (2021).
- 44. Ricote, S. & Bonanos, N. Enhanced sintering and conductivity study of cobalt or nickel doped solid solution of barium cerate and zirconate. *Solid State Ionics* **181**, 694–700 (2010).
- Ricote, S., Bonanos, N., Manerbino, A. & Coors, W. G. Conductivity study of dense BaCe<sub>x</sub>Zr <sub>(0.9-x)</sub>Y<sub>0.1</sub>O<sub>(3-δ)</sub> prepared by solid state reactive sintering at 1500 °C. *Int. J. Hydrogen Energy* **37**, 7954–7961 (2012).
- 46. Irvine, J. T. S., Sinclair, D. C. & West, A. R. Electroceramics: characterization by impedance spectroscopy. *Adv. Mater.* **2**, 132–138 (1990).
- Ebert, J. N., Jennings, D., Schäfer, L.-A., Sebold, D. & Rheinheimer, W. Bulk and grain boundary conductivity in doped BaZrO<sub>3</sub>: Bulk contribution dominates at operating temperatures. *Scr. Mater.* 241, 0–5 (2024).
- 48. Fleig, J., Rodewald, S. & Maier, J. Microcontact impedance measurements of individual highly resistive grain boundaries: General aspects and application to acceptor-doped SrTiO<sub>3</sub>. *J. Appl. Phys.* **87**, 2372–2381 (2000).
- 49. Gregori, G., Merkle, R. & Maier, J. Ion conduction and redistribution at grain boundaries in oxide systems. *Prog. Mater. Sci.* **89**, 252–305 (2017).
- Iguchi, F., Sata, N. & Yugami, H. Proton transport properties at the grain boundary of barium zirconate based proton conductors for intermediate temperature operating SOFC. *J. Mater. Chem.* 20, 6265–6270 (2010).
- 51. Kindelmann, M. *et al.* Segregation-controlled densification and grain growth in rare earth-doped Y<sub>2</sub>O<sub>3</sub>. *J. Am. Ceram. Soc.* **104**, 4946–4959 (2021).
- 52. Kim, D., Bliem, R., Hess, F., Gallet, J.-J. & Yildiz, B. Electrochemical Polarization Dependence of the Elastic and Electrostatic Driving Forces to Aliovalent Dopant Segregation on LaMnO<sub>3</sub>. *J. Am. Chem. Soc.* **142**, 3548–3563 (2020).
- 53. Yamazaki, Y., Babilo, P. & Haile, S. M. Defect chemistry of yttrium-doped barium zirconate: A thermodynamic analysis of water uptake. *Chem. Mater.* **20**, 6352–6357 (2008).
- 54. Jennings, D. *et al.* The Formation of Stacking Faults in Barium Zirconate-Type Perovskites. *Chem. Mater.* (2023) doi:10.1021/acs.chemmater.3c00787.
- 55. Hojo, H. *et al.* Atomic structure of a CeO<sub>2</sub> grain boundary: The role of oxygen vacancies. *Nano Lett.* **10**, 4668–4672 (2010).
- 56. M P Seah. Grain boundary segregation. J. Phys. F Met. Phys. 10, 1043 (1980).
- 57. Gömann, K. *et al.* Sr diffusion in undoped and La-doped SrTiO<sub>3</sub> single crystals under oxidizing conditions. *Phys. Chem. Chem. Phys.* 2053–2060 (2005) doi:10.1039/b418824a.
- 58. Koerfer, S., De Souza, R. A., Yoo, H. I. & Martin, M. Diffusion of Sr and Zr in BaTiO<sub>3</sub> single crystals. *Solid State Sci.* **10**, 725–734 (2008).

- 59. Hasle, I. *et al.* B-site cation inter-diffusion in yttrium substituted barium zirconate. *J. Mater. Chem. A* **9**, 21142–21150 (2021).
- Fabbri, E., Pergolesi, D., Licoccia, S. & Traversa, E. Does the increase in Y-dopant concentration improve the proton conductivity of BaZr<sub>1-x</sub>Y<sub>x</sub>O<sub>3-δ</sub> fuel cell electrolytes? *Solid State Ionics* 181, 1043–1051 (2010).
- 61. Gonçalves, M. D., Maram, P. S., Muccillo, R. & Navrotsky, A. Enthalpy of formation and thermodynamic insights into yttrium doped BaZrO<sub>3</sub>. *J. Mater. Chem. A* **2**, 17840–17847 (2014).
- 62. Cantwell, P. R. *et al.* Grain boundary complexions. *Acta Mater.* **62**, 1–48 (2014).
- 63. Bowman, W. J., Darbal, A. & Crozier, P. A. Linking Macroscopic and Nanoscopic Ionic Conductivity: A Semiempirical Framework for Characterizing Grain Boundary Conductivity in Polycrystalline Ceramics. *ACS Appl. Mater. Interfaces* **12**, 507–517 (2020).
- 64. Vahidi, H. *et al.* Which Interfaces Matter Most? A Non-monotonic Relationship between Grain Boundary Defect Chemistry and Ionic Conductivity in a Concentrated Solid Electrolyte. *ChemAxiv* (2024).
- 65. Babilo, P., Uda, T. & Haile, S. M. Processing of yttrium-doped barium zirconate for high proton conductivity. *J. Mater. Res.* 22, 1322–1330 (2007).
- 66. Yamazaki, Y., Hernandez-Sanchez, R. & Haile, S. M. High total proton conductivity in largegrained yttrium-doped barium zirconate. *Chem. Mater.* **21**, 2755–2762 (2009).
- 67. Bu, J., Jönsson, P. G. & Zhao, Z. Ionic conductivity of dense Ba $Zr_{0.5}Ce_{0.3}Ln_{0.2}O_{3-\delta}$  (Ln = Y, Sm, Gd, Dy) electrolytes. *J. Power Sources* **272**, 786–793 (2014).
- 68. Wang, M. *et al.* Improved Solid-State Reaction Method for Scaled-Up Synthesis of Ceramic Proton-Conducting Electrolyte Materials. *ACS Appl. Energy Mater.* **6**, 8316–8326 (2023).
- 69. Deibert, W. *et al.* Fabrication of multi-layered structures for proton conducting ceramic cells. *J. Mater. Chem. A* **3**, (2021).
- 70. Lyagaeva, J. G., Vdovin, G. K. & Medvedev, D. A. Distinguishing Bulk and Grain Boundary Transport of a Proton-Conducting Electrolyte by Combining Equivalent Circuit Scheme and Distribution of Relaxation Times Analyses. *J. Phys. Chem. C* **123**, 21993–21997 (2019).
- 71. Cheng, J., Luo, J. & Yang, K. Aimsgb: An algorithm and open-source python library to generate periodic grain boundary structures. *Comput. Mater. Sci.* **155**, 92–103 (2018).
- 72. Okhotnikov, K., Charpentier, T. & Cadars, S. Supercell program: a combinatorial structuregeneration approach for the local-level modeling of atomic substitutions and partial occupancies in crystals. *J. Cheminform.* **8**, 17 (2016).
- 73. Hohenberg, P. & Kohn, W. Inhomogeneous Electron Gas. Phys. Rev. 136, B864–B871 (1964).
- 74. Kohn, W. & Sham, L. J. Self-Consistent Equations Including Exchange and Correlation Effects. *Phys. Rev.* **140**, A1133–A1138 (1965).
- 75. Kresse, G. & Furthmüller, J. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. *Phys. Rev. B* **54**, 11169–11186 (1996).

- 76. Perdew, J. P., Burke, K. & Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **77**, 3865–3868 (1996).
- 77. Blöchl, P. E. Projector augmented-wave method. Phys. Rev. B 50, 17953–17979 (1994).
- 78. Fleig, J. The grain boundary impedance of random microstructures: numerical simulations and implications for the analysis of experimental data. *Solid State Ionics* **150**, 181–193 (2002).