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Non-Arrhenius grain growth in SrTiO₃: Impact on grain boundary conductivity and segregation

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ABSTRACT

In this study, a correlation between the conductivity, space charge layers, solute drag and non-Arrhenius grain growth in SrTiO₃ was investigated. Strontium titanate is known for its non-Arrhenius grain growth where grain growth rates decrease by orders of magnitude with increasing temperatures between 1350 °C and 1425 °C. Here, undoped SrTiO₃ was sintered and annealed at temperatures below and above the grain growth transition. The influence of the annealing temperature and time on the conductivity and space charge layers at grain boundaries (GBs) in SrTiO₃ was investigated by electrochemical impedance spectroscopy (EIS). STEM-EDS analysis indicates the presence of GBs with qualitative different cationic segregation in SrTiO₃. A distortion of the GB semi-circle in the impedance plots was found which was attributed to the presence of multiple GB types with different electric properties and space charge layers. The presence of two GB types as indicated by impedance analysis corresponds well with previous results, where solute drag and segregation was supposed to cause the non-Arrhenius grain growth behavior of SrTiO₃.

1. Introduction

Ceramic ionic conductors are important electrolyte materials for solid oxide fuel cells [1–5] and solid-state batteries [6–8]. In many cases, grain boundaries (GBs) are detrimental for the performance of the solid electrolytes due to their low conductivity. In perovskites and other oxide ceramics, the low conductivity of GBs is caused by space charge layers at the GBs [9–13]. In perovskites, space charge layers form because of the preferred formation of oxygen vacancies at GBs resulting in a positive GB core charge [12,14–17]. A potential difference between the GB and bulk material called the space charge potential ($\Delta\Phi$) is built up [17–20]. $\Delta\Phi$ is reduced by the segregation/accumulation of negative point defects (acceptor species) compensating the positive core charge. The depletion of charged defects in the space charge layer around the GB core further compensates the core charge [12,21,22].

Segregation and space charge layers might not only influence the electric properties of ceramic materials but also determine the microstructure evolution. The slow diffusion rate of the segregated cations at the GB can inhibit GB motion (solute drag) [23,24] and cause abnormal

grain growth (AGG) [14,17,23–33]. Yet, AGG can also be caused by other phenomena including nucleation barriers [34], GB anisotropy [35, 36], intergranular glassy films [34,37,38] or complexions [39–42]. AGG is observed in many perovskite materials relevant for energy or electronic applications, such as BaTiO₃ [43–45], lithium lanthanum titanate (LLTO) [45], PZT [46], BNT-BT [47] and KNN [48–50], and sometimes poses a critical issue for the application e.g., for multilayer ceramic capacitors [51].

In the case of SrTiO₃, AGG was suggested to be related to solute drag effects [45] which originate from segregation and space charge layers at GBs. Additionally, in SrTiO₃ AGG is accompanied by a grain growth transition where grain growth rates decrease by about two orders of magnitude with increasing temperatures between 1350 °C and 1425 °C [33,45,52]. When the bimodal microstructure evolution of SrTiO₃ was quantified [32], it was argued that the grain growth transition is caused by the co-existence of two different GB types with different migration rates [24,32,33,45,52,53]. At low temperature (≤ 1350 °C) grain growth in SrTiO₃ is dominated by fast GBs [52] since most grains are surrounded by a majority of these fast GBs. The result is homogeneous or normal

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grain growth at temperature below 1350 °C. If the temperature increases above 1350 °C the number of fast GBs decreases with increasing temperature [32]. The grain growth kinetics of SrTiO₃ become dominated by slow GBs. Grains that are surrounded by the slow GBs barely grow, while grains with enough fast GBs adjacent to them can grow fast. The grain growth kinetics of SrTiO₃ become heterogeneous or abnormal above 1350 °C. Most of the fast GBs are then adjacent to the abnormal/large grains while most of the slow-migrating GBs are adjacent to the normal/small grains. Not only the GB mobility but also the driving force for grain growth determines the grain growth behavior of a single grain because the driving force for grain growth depends on the size difference of said grain and its nearest neighbors [54,55].

Generally, solute drag can also result in the co-existence of two different GB configurations [23,29,56–58] instead of being caused by them. While GBs with cationic segregation are dragged by cations slow diffusion, very high driving forces can result in non-equilibrium GBs with less or no cationic segregation (break-away in the solute drag model). Accordingly, if solute drag is responsible for AGG in SrTiO₃, there should exist two GB types with different segregation profiles and space charge layers. Solute drag might not even depend on segregation and space charge but might also be able to influence segregation and space charge layer. Recent grain growth simulations [14], where the GB core charge and space charge layers were tracked during GB migration indicate a change in space charge potential with migration rate. The non-equilibrium boundaries with less cationic segregation after break-away have more space charge (i.e., less conductivity) compared to the near-equilibrium boundaries that experience solute drag. Note that the non-dragged state can be regarded as non-equilibrium state of solute drag. After prolonged grain growth non-dragged GBs will agglomerate solutes during migration and slow down, approaching the dragged composition again.

The existence of different GB types in SrTiO₃ was investigated by S-TEM [59,60]. The results were not conclusive, because the GB anisotropy results in considerable scattering of GB configuration and chemistry, and the statistics were probably not sufficient to clearly observe the changes. Still, ignoring the structural differentiation of GBs in [59,60], small grains are more frequently surrounded by GBs with Ti excess. Possibly, this Ti excess causes diffusional drag similar to solute drag. Whether the Ti-rich GBs were truly Ti-rich or Sr-deficient could not be identified in [57,58].

This study investigates the impact of microstructure evolution on the GB conductivity of the model material SrTiO₃ and investigates the co-existence of multiple GB types in SrTiO₃. Annealing conditions of undoped SrTiO₃ ceramics were chosen with the grain growth transition of SrTiO₃ in mind, covering the transition temperature range, as well as temperatures above and below. The resulting microstructures agree with previously reported microstructures of SrTiO₃. Scanning Transmission Electron Microscopy (S-TEM) combined with Energy Dispersive X-ray Spectroscopy (EDS), and Electrochemical Impedance Spectroscopy (EIS) were used to characterize GB properties. The focus is on cationic segregation (STEM-EDS), space charge potentials and GB conductivity (EIS). The results are discussed in the framework of non-Arrhenius grain growth, solute drag and space charge to correlate microstructure evolution and electrical properties of SrTiO₃.

The authors emphasize that the correlations found between segregation, space charge layer, grain growth kinetics and GB conductivity are not conclusive. This is due to the nature of the characterization methods used: S-TEM EDS is a very local and microscopic technique, EIS is an averaging macroscopic technique and SEM imaging is a mesoscopic analysis method. While the data show significant experimental evidence, it is not possible to conclusively show the interplay of grain growth and grain boundary conductivity. To the authors' knowledge there is no set of methods that will provide a complete data set on GB properties in a polycrystal. The authors therefore advise to read the current manuscript and interpret the data with care and the difficulty in correlation in mind.

The possible interdependence of microstructure evolution and conductivity can be used as a pathway to tailor functional properties of SrTiO₃ by well-chosen thermal treatments, and as this material is a prototype for the class of perovskites, the findings are relevant to many important functional ceramics such as BaTiO₃ and BaZrO₃.

2. Experimental procedure

2.1. Sample preparation

Undoped SrTiO₃ powders were synthesized by the mixed oxide/carbonate route using high purity raw materials, high-energy ball milling and calcination at 975 °C [22]. Green bodies were uniaxially pressed in a stainless-steel pressing die with a diameter of 10 mm with an applied force of 2 kN. Stearic acid was used as lubricant during pressing. The green bodies were further densified at a pressure of 400 MPa for 2 min using a cold-isostatic press. The green bodies were pre-sintered at 1425 °C for 1 h in air and subsequently annealed either for a constant time at varying temperature or at constant temperature for varying times. Samples were annealed at 1350 °C, 1370 °C, 1400 °C, 1425 °C, 1460 °C, and 1500 °C for 5 h. Additionally, other samples were annealed at either 1500 °C for 0.5 h, 2 h and 5 h or at 1350 °C for 2 h, 5 h and 10 h. These two temperatures were chosen since SrTiO₃ has about the same grain growth constant for both temperatures; yet at 1350 °C (below the grain growth transition), normal grain growth (NGG) occurs, and at 1500 °C (above the grain growth transition) abnormal grain growth occurs. All heating and cooling rates were set to 10 K/min.

2.2. Microstructure analysis

For microstructure analysis, the annealed samples were cold-molded in Epoxy 2000 and then prepared by grinding and polishing. The polished samples were contacted with conductive copper tape and sputtered with a 6 nm thick Pt layer. The microstructures were analyzed with a Zeiss EVO 15 SEM (Zeiss, Germany) using an acceleration voltage of 8 kV at a working distance of 8.5 mm. Both secondary electron (SE) and back scatter electron (BSE) images were taken. The average grain sizes were determined with the line intercept method at min. 300 grains. Minor secondary phases were found and analyzed using an Ultim Max 100 energy dispersive x-ray spectroscopy EDS (Oxford Instruments, UK).

2.3. GB characterization with STEM

Two different annealing temperatures were selected for scanning transmission electron microscopy (STEM) analysis i.e., 1350 °C and 1500 °C. Samples for STEM analysis were prepared either with a conventional preparation method, or by the focused ion beam (FIB) lift-out method. Conventional samples were made by a standard mechanical polishing and dimpling procedure, followed by ion milling (with a final milling energy of 0.2 kV) in a Gatan Precision Ion Polishing System II (PIPS II). A FEI Helios NanoLab 460F1 was used to take a lift-out containing a GB between two large grains in the sample annealed at 1500 °C. The final milling energy for FIB lamella preparation was 2 kV.

A Hitachi HF5000 S/TEM was utilized for high angle annular dark field (HAADF) imaging and energy dispersive x-ray spectroscopy (EDS). EDS data analysis was done with Hyperspy [61]. EDS maps and line scans were quantified using a standardless (Cliff-Lorimer) quantification method. K-factors for quantification were taken assuming that the overall composition of the EDS map is equivalent to the as-prepared composition of the sample.

GBs analyzed by STEM-EDS were categorized into Sr-rich, stoichiometric and Ti-rich using the logic argument in Eq. (1) [59]. There, $\sigma_{\text{Sr/Ti, grain}}$ is the standard deviation of the Sr:Ti ratio in grain adjacent to the analyzed GB, $E_{\text{EDX,GB}}$ is the error in measurement of the Sr:Ti ratio (≈ 0.05), the parameter $r_{\text{Sr/Ti, GB}}$ is the Sr:Ti ratio in the GB core and

$\bar{r}_{\text{Sr}/\text{Ti, grain}}$ is the average Sr:Ti ratio in the adjacent grains. In short that means if the GB composition was measured to be off-stoichiometric by more than the assumed measurement error (0.05), then the GB was classified as Sr- or Ti-rich. Otherwise, the composition was classified as neutral.

$$\begin{aligned} &\text{if } \left(\frac{r_{\text{Sr}}}{\text{Ti}}_{\text{GB}} - E_{\text{EDX,GB}} \right) > \left(\bar{r}_{\text{Sr}}_{\text{Ti,grain}} + \sigma_{\text{Sr}}_{\text{Ti,grain}} \right) = \text{true} \rightarrow \text{GB is Sr rich or Ti deficient} \\ &\text{elseif } \left(\frac{r_{\text{Sr}}}{\text{Ti}}_{\text{GB}} + E_{\text{EDX,GB}} \right) < \left(\bar{r}_{\text{Sr}}_{\text{Ti,grain}} - \sigma_{\text{Sr}}_{\text{Ti,grain}} \right) = \text{true} \rightarrow \text{GB is Sr deficient or Ti rich} \\ &\text{else} \rightarrow \text{GB is neutral} \end{aligned} \quad (1)$$

2.4. Impedance analysis

Samples for impedance analysis were ground to the desired thickness of 1 mm using SiC abrasive paper with a grit of 400, 800 and 1200. The as prepared impedance samples were then sputtered with Pt and the coated with Pt-paste. The Pt-paste was dried at 60 °C for 1 h and then burned onto the samples at 900 °C for 2 h. The heating and cooling rate was adjusted to 10 K/min.

The samples' electrical properties were analyzed by electrochemical impedance spectroscopy using an Alpha-A high frequency analyzer (Novocontrol Technologies GmbH & Co. KG, Germany). The measurements were performed at a temperature range between 600 °C and 400 °C in 12.5 K steps and in a frequency range from 10 MHz to 100 mHz in air at ambient pressures. The measurement results were evaluated and fitted using the RelaxIS software (rhd instruments, Germany). An equivalent circuit designed according to the brick-layer model [62–65] was utilized for fitting the data. For ceramics a typical equivalent circuit consists of 3 RQ-circuits in series [62]. The RQ-circuits represent the grain bulk, GB and sample-electrode-interface. A RQ-circuit consists of a resistor and constant phase element connected in parallel. The electric response of Pt-electrodes on SrTiO₃ is at very low frequencies and was minor in the frame of this study. To keep the analysis simple, the respective frequency part was excluded from the fitting procedure if an electrode contribution was visible at higher temperatures or for samples with low resistance [66,67]; accordingly, the RQ circuit for the electrodes was omitted. The designing process of the equivalent circuit is further elaborated on in section 3.2. The bulk conductivity σ_{Bulk} and GB conductivity σ_{GB} were determined according to equation 2 and equation 3 respectively.

$$\sigma_{\text{Bulk}} = \frac{1}{R_{\text{Bulk}}} \cdot \frac{l}{A} \quad (2)$$

$$\sigma_{\text{GB}} = \frac{1}{R_{\text{GB}}} \cdot \frac{l}{A} \cdot \frac{C_{\text{Bulk}}}{C_{\text{GB}}} \quad (3)$$

R_{Bulk} corresponds to the total bulk resistance, R_{GB} to the total GB resistance, l to the sample thickness, A to the sample's or electrode's cross-sectional area and C_{Bulk} and C_{GB} correspond to the bulk and Gb capacitance respectively.

2.5. Space charge characterization

Space charge width and potential were obtained by evaluating the

samples' impedance data using the Mott-Schottky equation [15,68]. Other methods for the evaluation of space charge thickness such as the plate capacitor equation [66,69–71] can also be used. Yet, this approach when applied to the data in this study resulted in less temperature stability for the GB thickness and wrong sizes for average grain sizes. Evaluation based on the Mott-Schottky model uses defect chemistry

models and the space charge potential ($\Delta\Phi$) of GBs to obtain space charge thicknesses (λ_{MS}). The space charge potential ($\Delta\Phi$) is obtained by numerically solving equation 4 [15,72–74], where τ_{GB} and τ_{bulk} are the relaxation times of the samples' GB and bulk material respectively, e the elementary charge, k_b the Boltzmann constant and T the temperature of the EIS measurement in (K).

$$\frac{\tau_{\text{GB}}}{\tau_{\text{bulk}}} = \frac{\exp\left(\frac{e\Delta\Phi}{k_b T}\right)}{2e\Delta\Phi} \cdot k_b T \quad (4)$$

The relaxation time of bulk and grain boundary are the relaxation times of the respective RQ-circuits. The relaxation time of a RQ-circuit can be calculated from its resistance and capacitance i.e., the resistance and capacitance of the bulk or GB.

$$\tau_{\text{RQ}} = 2\pi \cdot RC \quad (5)$$

Uncertainties and errors in the evaluation process for space charge potentials are reduced by using the relaxation times of bulk (τ_{bulk}) and GBs (τ_{GB} , equation 4) instead of resistance or capacitance ratios [74]. Also, before using this approach the resistance and capacitance of the bulk named GB have to be known, for example from fitting the impedance data using an equivalent circuit.

To calculate the space charge, thickness λ_{MS} the space charge potential $\Delta\Phi$ and the Debye length λ_{Debye} (high temperature space charge thickness) have to be known. The λ_{Debye} is a quantity describing the thickness of a space charge layer in which all defects are mobile. λ_{Debye} is wholly dependent on the samples defect chemistry (equation 5) [15,75].

$$\lambda_{\text{Debye}} = \sqrt{\frac{\epsilon_0 \epsilon_r k_b T}{2e^2 \cdot c_{\text{major}}}} \quad (6)$$

The majority defect concentration (c_{major}) of mobile defects in the bulk has to be known. In this study the concentration of the majority defect was assumed to be in the order of 10^{18} cm^{-3} which is used in literature on simulation of space charge layers in undoped SrTiO₃ ceramics [76]. In equation 6, ϵ_0 is the permittivity of the vacuum and ϵ_r the relative permittivity of SrTiO₃ [12,77]. The permittivity of SrTiO₃ is calculated using the equation 7.

$$\epsilon_r(\text{STO}) = \frac{97900}{T} \quad (7)$$

With knowledge on the Debye length (λ_{Debye}) and space charge potential ($\Delta\Phi$), the space charge thicknesses based on the Mott-Schottky model (λ_{MS}) is obtained by Eq. (8) [15,72–74].

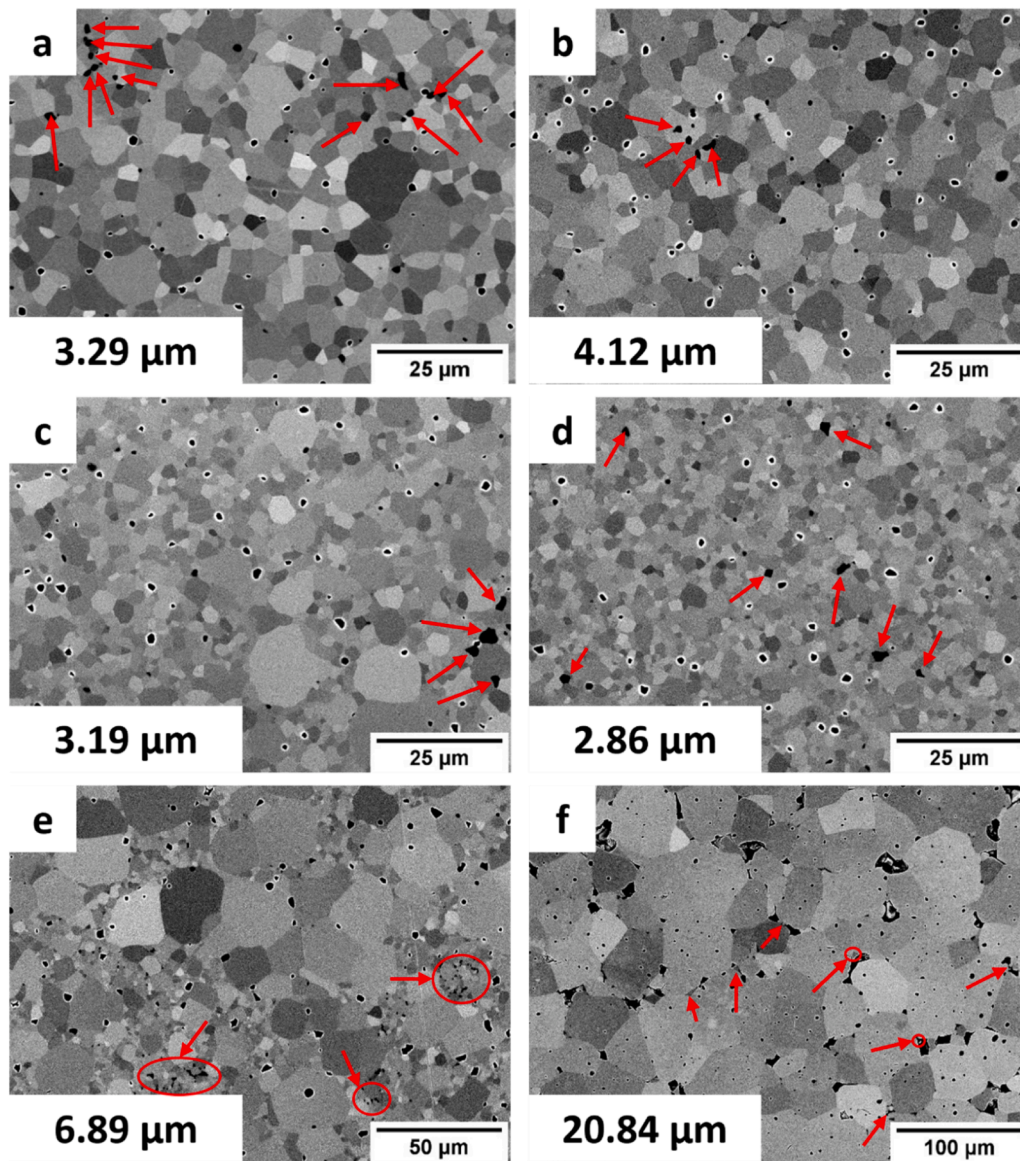


Fig. 1. BSE-SEM microstructure images of samples annealed at a) 1350 °C, b) 1370 °C, c) 1400 °C, d) 1425 °C, e) 1460 °C and f) 1500 °C for 5 h each. Note the different scales of e and f.

$$\lambda_{\text{MS}} = \lambda_{\text{Debye}} \cdot \sqrt{\frac{4e\Delta\Phi}{k_b T}} \quad (8)$$

The impedance data used to calculate the relaxation times of the bulk and GBs, i.e., the space charge potentials were obtained at temperatures at which cationic diffusion can be regarded as frozen-in. Consequently, the MS model fits the GBs' defect chemistry present during the EIS measurements better than the Debye model. Note that the segregation profile of acceptor impurities as postulated by the Mott-Schottky model is most-likely incorrect. The true cationic segregation profile at the grain boundary probably resembles the equilibrium state of the grain boundary at the temperatures at which cationic defects become immobile.

3. Results and discussion

3.1. Microstructure evolution

SEM images of undoped SrTiO₃ samples' microstructures annealed at different temperatures for 5 h are shown in Fig. 1. The high contrast of

the BSE images stems from channeling contrast due to the crystal orientation which is pronounced in SrTiO₃. Samples annealed at 1400 °C and 1460 °C have bimodal microstructures (Fig. 1c, e), while samples annealed at 1350 °C, 1370 °C and 1425 °C have unimodal microstructures (Fig. 1a, b, d). After annealing at 1500 °C (Fig. 1f), the microstructure likely went through a stage of abnormal grain growth, and primarily consists of impinging abnormal grains and is again unimodal. The average grain sizes of each sample agree with grain growth constants previously reported for undoped SrTiO₃ showing non-Arrhenius grain growth [32,33,52]. Only samples annealed at 1350 °C for 5 h have smaller average grain sizes (3.29 μm) than expected (5.0 μm to 5.5 μm).

SEM images of undoped SrTiO₃ samples annealed at 1350 °C for 2 h, 5 h and 10 h as well as samples annealed at 1500 °C for 0.5 h, 2 h and 5 h are depicted Figure 2. Samples annealed at 1350 °C experience NGG with steadily increasing grain sizes from 3.9 μm after 2 h to 9.0 μm after 10 h of annealing (Fig. 2b,d,f). Samples annealed at 1500 °C show clear signs of AGG (Figure 2 a,c,e). The AGG in samples annealed at 1500 °C results in a sharp increase in average grain size from 3.14 μm after 0.5 h to 20.84 μm after 5 h. In this study, the overall grain size of annealed

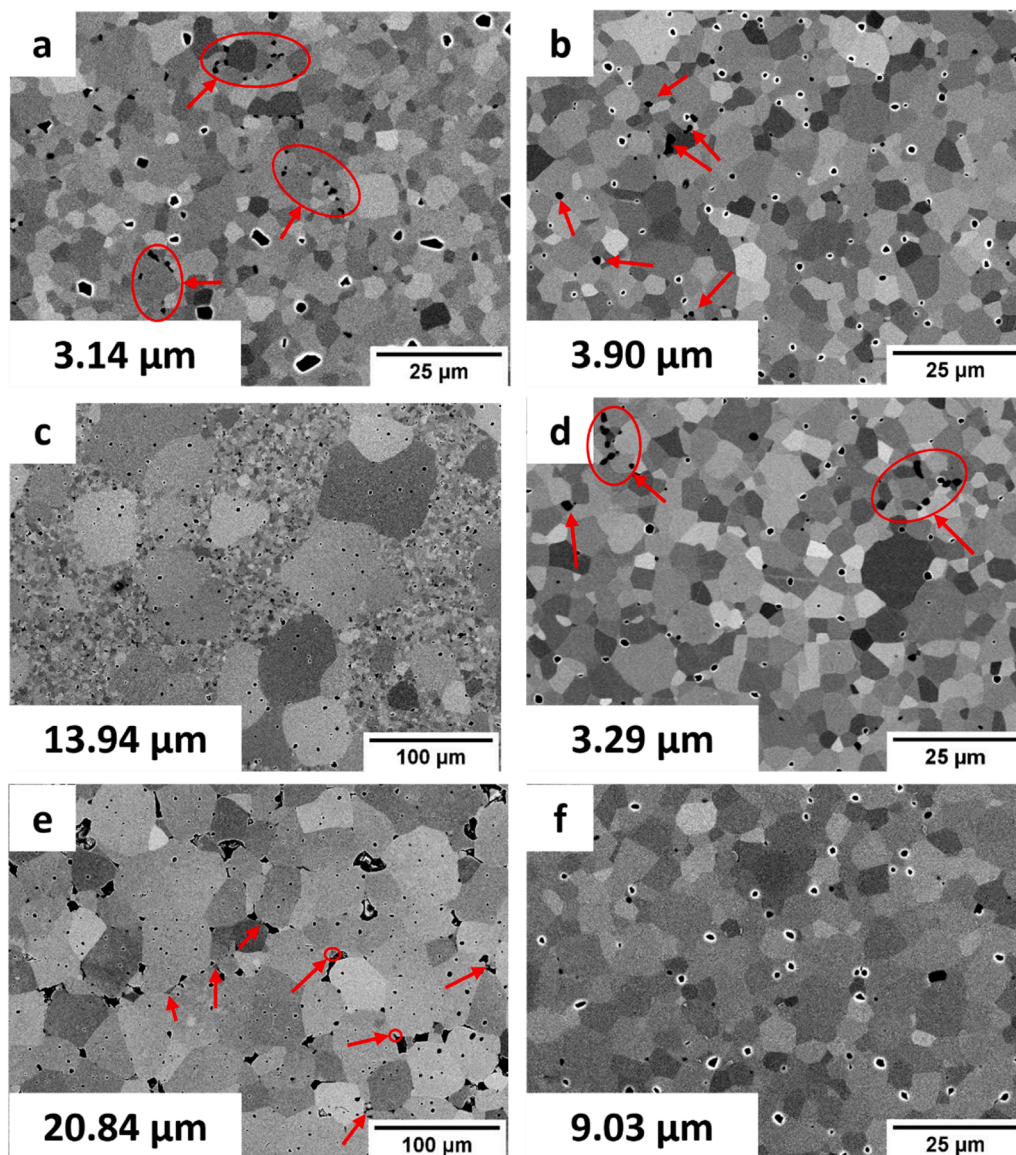


Fig. 2. : BSE-SEM microstructure images of undoped SrTiO_3 samples annealed at 1500°C for a) 0.5 h, c) 2 h and e) 5 h and of samples annealed at 1350°C for b) 2 h, d) 5 h and f) 10 h. Note the different scales in c and e.

SrTiO_3 samples agrees well with expected grain sizes with one exception (1350°C for 5 h).

Some SEM images in Fig. 1 and Figure 2 show small amounts of secondary phases which were analyzed with EDS and found to be Ti-rich secondary phases (Figure S3). These types of secondary phases are typical for undoped SrTiO_3 with a slight B-site excess [78]. XRD diffraction patterns of the samples show the cubic perovskite phase of SrTiO_3 with no secondary peaks coinciding with the main peaks of TiO_2 rutile phase, indicating that the amount of secondary phase is below 1 % for each sample.

3.2. Impedance of undoped SrTiO_3

Electric properties were analyzed by electrochemical impedance spectroscopy (EIS) analysis (see Sections 2.4 and 2.5). The Nyquist impedance plot of undoped SrTiO_3 pre-sintered at 1425°C for 1 h is shown in Fig. 3. The impedance plot shows a small semi-circle corresponding to the grain bulk in the high frequency part and a large semi-circle representing the GB in the medium to low frequency part. The GB semi-circle is notably distorted. The distortion of the GB signal becomes

more prevalent as the measurement temperature increases (Fig. 5). Impedance data was first fitted using an equivalent circuit with 2 RQ-circuits; yet the quality of the fit was lacking (Fig. 3 dashed grey curve). For that reason, the equivalent circuit was extended with one additional RQ-circuit. The new fit (Fig. 3 grey curve) agrees well with the impedance data (Fig. 3 grey crosses). Distorted impedance semi-circles were observed for every sample in this study, and a series of three RQ-circuits was subsequently used as equivalent circuit for every sample. The first RQ-circuit represents the bulk (RQ_1 in Fig. 3) while the two other RQ-circuits (RQ_2 and RQ_3 in Fig. 3) represent the GB response. The second RQ-circuit (RQ_2 , blue semi-circle) is the newly added RQ-circuit to accommodate the distortion of the GB semi-circle.

Shoulders or distorted semi-circles in impedance plots of undoped SrTiO_3 have been reported in the literature and were fitted with similar equivalent circuits as in this study [71], yet no cause for this phenomenon had been identified. Maier et al. have done extensive work in modeling the electrochemical response of non-ideal microstructures and phenomena that can lead to similar responses [79,80,73,74,81,82]. Their simulations revealed that most deviations from the cubic grain shape of the brick layer model change the GB impedance when

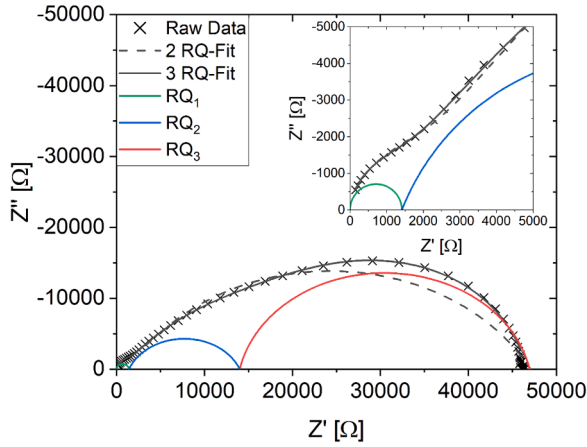


Fig. 3. Impedance data of an undoped SrTiO₃ sample pre-sintered at 1425 °C for 1 h and measured at 600 °C together with the fit-curves using 2 RQ-circuits (dashed grey) and 3 RQ-circuits (grey) as equivalent circuit. The three semi-circles of RQ₁ (green), RQ₂ (blue) and RQ₃ (red) represent the impedance response of the grain bulk, GB₁ and GB₂ respectively.

compared to the brick layer model [80,82]. Further simulations indicated that the current density is higher in large grains than in small grains [79,74]. In the most extreme case, a current path through networks of large grains can exist in bimodal microstructures since these networks have a lower GB density and by that a lower resistance than the surrounding material (small grains, high GB density) [74]. In particular, two co-existing types of GBs with distinctively different conductivities result in distorted semi-circles [79,80]. In all of these cases, the distortion is caused by inhomogeneous current density distribution, which can lead to additional relaxation effects being visible as

additional or distorted semi-circle in the impedance plot [79,80]. Fig. 4 shows a schematic of inhomogeneous current distributions at a highly resistive element as e.g., an individual GB (Fig. 4a), percolation effects in bimodal microstructures (Fig. 4b) and conduction around highly resistive GBs (Fig. 4c).

The presence of multiple distinct GB types with largely different conductivities seems to be the most likely cause for the distorted impedance semi-circle in Fig. 3. This would fit previous observation for SrTiO₃ as Sr-rich, Ti-rich and neutral GBs are known to be present simultaneously from TEM investigations [59,60]. Additionally, AGG in SrTiO₃ is thought to be caused by the existence and co-existence of two GB types with different migration rates [24,31–33,45,52,53]. The difference in migration rate was explained by solute drag [14,17,24,31–33], resulting in two GB types with different segregation and space charge layers.

The authors propose that the two boundary types observed during grain growth [24,32,33,45,52,53] correspond to the ones observed by EIS in this study. The two GB types represented by RQ₂ and RQ₃ (see

Table 1

Resistance R , capacitance C , relaxation frequency f , space charge thickness λ_{MS} , space charge potential $\Delta\Phi$, specific conductivity $\sigma_{specific}$ and activation energy of conduction E_a obtained by evaluating fit data of the impedance plot in Fig. 3. The impedance plot of undoped SrTiO₃ measured at 600 °C was fitted with a series of 3 RQ-circuits as equivalent circuit.

Feature	Bulk	GB ₁	GB ₂
R [Ω]	1415	12,593	32,956
C [F]	$5.2 \cdot 10^{-11}$	$2.3 \cdot 10^{-10}$	$9.7 \cdot 10^{-10}$
f [Hz]	$2.1 \cdot 10^7$	$5.4 \cdot 10^4$	$5.0 \cdot 10^3$
$\sigma_{specific}$ [S/cm]	$3.3 \cdot 10^{-4}$	$8.1 \cdot 10^{-6}$	$7.5 \cdot 10^{-7}$
E_a [eV]	1.4	0.7	2.0
λ_{MS} [nm]	–	37	48
$\Delta\Phi$ [eV]	–	0.24	0.39

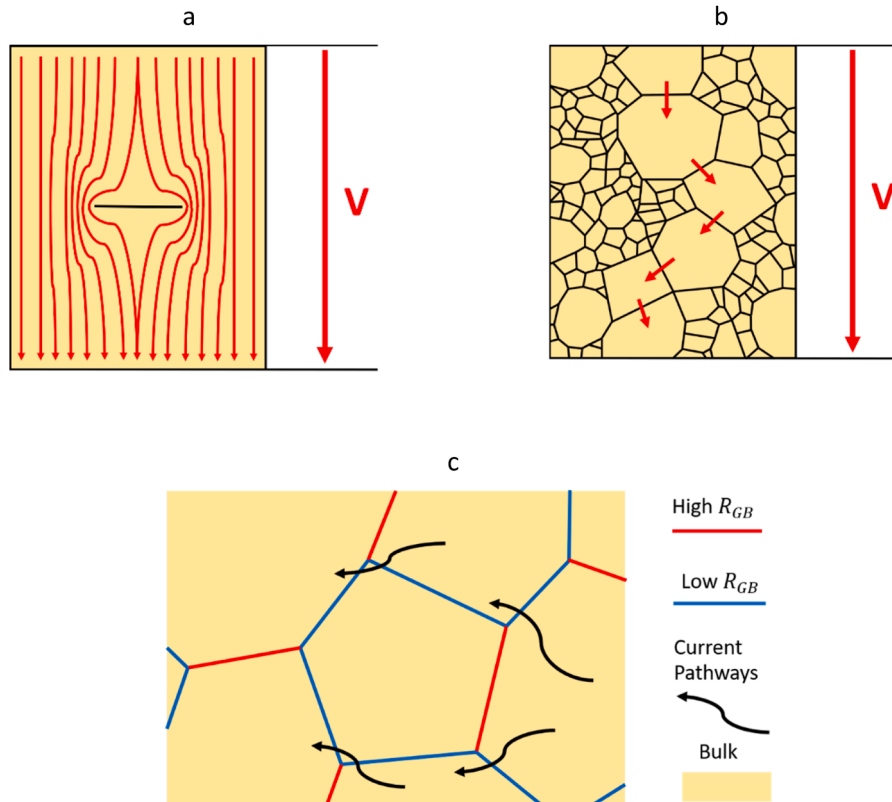


Fig. 4. a) Current constriction effects around a high resistivity area in a sample, b) current conduction due to percolation through abnormal grains (areas of low GB density) and c) redirection of the current flow around highly resistive GBs.

Fig. 3) will from here on be referred to as GB₁ and GB₂ respectively. Note that this is a simplification as the GB properties scatter and do not fall into two sharply separated categories, but likely a broad non-Gaussian GB property distribution with two maxima [79]. Yet from here, we will assume the presence of two distinct GB types without a property distribution. Table 1 shows the parameters of a fit of the impedance data in Fig. 3 and its evaluation, detailing the electric properties of the two GB types.

The two GB types (GB₁ and GB₂) have distinguishable properties. The resistance value (R) and capacitance (C) value of GB₁ are smaller by a factor of two to four when compared to the same values of GB₂. Because of these small differences, the relaxation frequency (f) of both GB types differs by one order of magnitude, clearly separating them. The specific conductivity (σ_{specific}) of GB₁ and GB₂ also differ by one order of magnitude and are about two orders of magnitude lower than the bulk. The activation energy (E_a) of bulk conductivity is slightly higher than the expected value of 1 eV and lower [42,77,83] while that of GB₂ is higher than the expected value for GBs in SrTiO₃ [42,66,77,81]. The activation energy of GB₁ on the other hand is lower than that of even the bulk and differs from that of GB₂ by more than a factor of two. The space charge thickness (λ_{MS}) of GB₁ is thinner than that of GB₂ and also shows a lower space charge potential ($\Delta\Phi$). The lower space charge potential, being about half that of GB₂, can also explain the lower resistance, activation energy, and higher conductivity of GB₁ when compared to GB₂. All of these observations hold true for any measurement presented in this study (Section 3.4). The resistance and capacitance of both GB types vary depending on annealing temperature and time. Nonetheless, both GB types can be clearly distinguished from one another based on their relaxation frequency, conductivity, and space charge potentials, which in most cases differ at least by one order of magnitude (f and σ) or by a factor of two ($\Delta\Phi$).

3.3. Dependence of impedance on annealing time and temperature

Undoped SrTiO₃ samples were annealed at varying temperatures for 5 h to investigate the impact of annealing temperature on the electrical properties of SrTiO₃. Electrical properties were measured using electrochemical impedance spectroscopy. Normalized Nyquist impedance plots of those samples' impedance are shown in Fig. 5. The inset in Fig. 5 was added to better visualize the high frequency part of the impedance plot and the Nyquist plot of the sample annealed at 1500 °C.

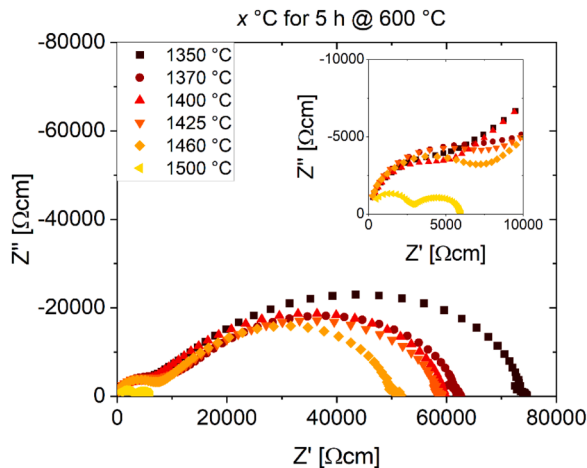


Fig. 5. Normalized Nyquist impedance plots of undoped SrTiO₃ samples annealed at 1350 °C, 1370 °C, 1400 °C, 1425 °C, 1460 °C and 1500 °C for 5 h each. The inset shows a smaller impedance range to better resolve the bulk response and the small Nyquist plot of the sample annealed at 1500 °C. The impedance data of each sample were measured at 500 °C and standardized to the samples' dimensions.

The total impedance of samples annealed between 1350 °C and 1500 °C for 5 h decreases steadily with increasing annealing temperature. The greatest decrease occurs between samples annealed at and 1460 °C and 1500 °C. This can easily be explained by an increase in grain size with increasing annealing temperature. Grain growth in SrTiO₃ is known to slow down in the temperature range between 1350 °C and 1425 °C [32, 60]; that means that the average grain size decreases with increasing annealing temperature. Yet, still a slight decrease in total impedance is observed for this temperature range (1370 °C to 1425 °C) even though an increase in total impedance would be expected based on the samples' average grain sizes (Fig. 1). No significant changes in the bulk's impedance are observed between 1350 °C and 1460 °C. The change in total impedance is thereby caused by the GB impedance. As mentioned in the previous section 3.2 the impedance signal of undoped SrTiO₃ features a distorted GB impedance arc which was explained by the presence of two GB types with distinct electrochemistry i.e., space charge layer composition. The unexpected changes in the total impedance of undoped SrTiO₃ samples between 1370 °C and 1425 °C might be caused by changes in the space charge layers due to grain growth or the population density of the two GB types (see a more detailed explanation in the bullet points below). The sample annealed at 1500 °C also features a strong decrease in grain bulk impedance compared to the other samples that were annealed for 5 h (Fig. 5 inset). It is not clear why the bulk response of the sample annealed at 1500 °C is half of that of the other samples. A possible explanation are changes in SrTiO₃'s bulk defect chemistry at such high annealing temperatures.

To investigate the time dependence of SrTiO₃'s impedance, two temperatures (1350 °C and 1500 °C) were chosen based on the non-Arrhenius grain growth behavior of SrTiO₃. The grain growth rate is similar for both temperatures [32], yet at 1350 °C NGG and at 1500 °C AGG occurs. The normalized Nyquist impedance plots of undoped SrTiO₃ samples annealed at 1350 °C for 2 h, 5 h and 10 h and 1500 °C for 0.5 h, 2 h and 5 h are shown in Fig. 6.

The impedance of samples annealed at 1350 °C increases with increasing annealing time (Fig. 6a). Since the grain size increases from about 3 μm to 9 μm for these samples, a decrease in total impedance due to a decrease in GB density is expected; accordingly, the observed behavior is counterintuitive. The impedance of samples annealed at 1500 °C behaves more intuitively where the total impedance decreases with increasing annealing time and grain size.

The changes in impedance of samples annealed at 1350 °C or of samples annealed between 1370 °C and 1425 °C for 5 h cannot be easily explained by grain growth, changes in grain size distribution, grain shape or percolation effects (see section 3.2). We suspect changes in GB properties to be responsible for these changes and propose three possible explanations:

- (1) The GB chemistry changes during grain growth. Defects are known to segregate towards GBs in SrTiO₃ forming space charge layers at GBs that decreases GB conductivity (Section 1). The segregated defects also slow down grain growth by solute drag (Section 1). Simulations of segregated defects predict changes in space charge thickness, potential and defect concentration for migrating GBs [14]. The changes depended on the migration speed of the moving GB with slow GBs experiencing barely any changes and fast-moving GBs experiencing a decrease in defect segregation and space charge potential. It is known that grain growth slows down for extended annealing times either due to a decrease in driving force or an accumulation of defects at the GBs. This effect is enhanced at high annealing temperature due to faster migration speeds which can even cause stagnation in grain growth [24,33]. Subsequently, annealed SrTiO₃ samples should also feature space charge potentials and thicknesses varying with annealing temperature and time (see section 3.4).
- (2) The number and fraction of the two GB types (section 3.2) changes with annealing temperature and time. The non-

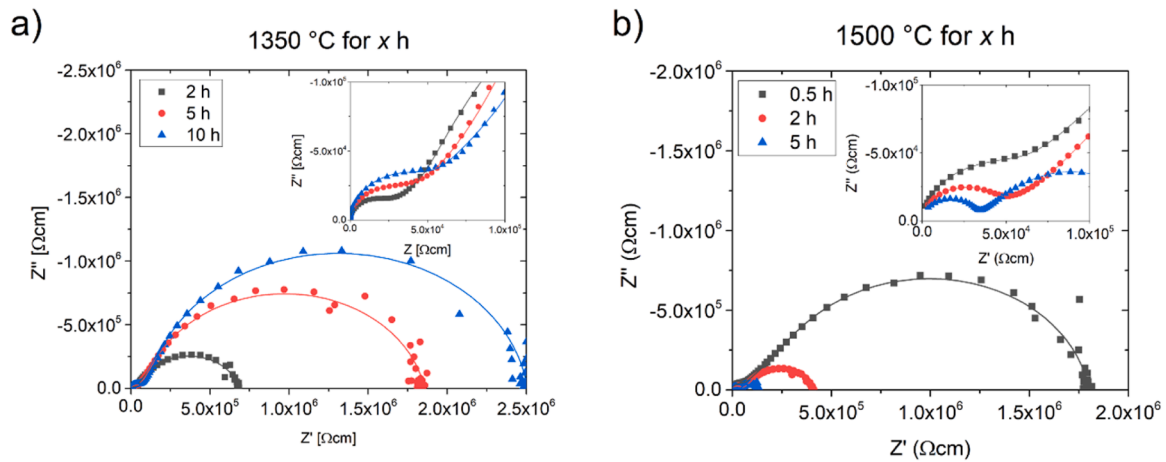


Fig. 6. Normalized Nyquist impedance plots of undoped SrTiO₃ samples annealed at 1350 °C for 2 h, 5 h and 10 h (a) and standardized Nyquist impedance plots of undoped SrTiO₃ samples annealed at 1500 °C for 0.5 h, 2 h and 5 h. The insets show the bulk responses for a smaller impedance range. The impedance data were measured at 500 °C and standardized to the samples' dimensions.

Arrhenius grain growth behavior was previously explained by the presence of two types of GBs with different mobilities [24,32,52]. At low annealing temperatures, the high mobility GB type dominates the grain growth while at higher annealing temperatures the low mobility GB type does. Subsequently, if one GB type predominantly migrates while the other type barely migrates, their number should change with different rates during annealing [32].

- (3) The defect chemistry changes with annealing temperature and, accordingly, the GB properties. Segregation profiles at GBs are determined by the bulk defect concentration and the bulk's defect concentration is dependent on oxygen partial pressure $P(O_2)$ and temperature [84–86]. An increase in temperature results in an overall increase in the bulk's point defect concentration. Also, the mechanism of charge compensation for charge neutrality may change with increasing temperature similar to a reduction in $P(O_2)$. For that reason, annealing temperature might have an impact on the GB chemistry and structure in SrTiO₃.

The changes in segregation profile due to GB migration (1) will be further discussed in section 3.4. The influence of changes in the frequency ratio of GB₁ and GB₂ (2), and varying bulk defect concentration on the GB chemistry (3) cannot conclusively be confirmed with the data presented in this study.

3.4. Space charge thickness and potential

The changes in the impedance of SrTiO₃ with annealing conditions were correlated to changes in the space charge thickness and potential.

Table 2

Space charge thickness and potential evaluated based on the Mott-Schottky model (MS) for both GB types (GB₁ & GB₂). The data are based on experimental impedance measurements of samples annealed at temperatures between 1350 °C and 1500 °C for 5 h. The measurements were performed at 500 °C.

Temperature [°C]	Space charge thickness λ_{MS} [nm]		Space charge potential $\Delta\Phi$ [eV]	
	GB ₁	GB ₂	GB ₁	GB ₂
1350	58	92	0.13	0.33
1370	57	103	0.12	0.40
1400	63	96	0.16	0.37
1425	60	98	0.14	0.38
1460	62	101	0.15	0.40
1500	73	94	0.26	0.35

Table 3

Space charge thicknesses and potentials of undoped SrTiO₃ samples depending on annealing time for both GB types (GB₁ & GB₂). The space charge thicknesses and potentials were evaluated according to the Mott-Schottky model. The data are based on experimental impedance measurements performed at 500 °C.

Temperature [°C]	Time [h]	Space charge thickness λ_{MS} [nm]		Space charge potential $\Delta\Phi$ [eV]	
		GB ₁	GB ₂	GB ₁	GB ₂
1350	2	70	99	0.19	0.39
	5	58	92	0.13	0.33
	10	62	95	0.15	0.37
1500	0.5	73	94	0.21	0.35
	2	64	97	0.16	0.37
	5	73	94	0.26	0.35

The evaluation of space charge layers was based on the Mott-Schottky model. Resistance and capacitance values of the bulk and GBs were obtained by fitting the impedance data with the equivalent circuit discussed in section 3.2. In Table 2 data on the space charge layers of samples annealed for 5 h at different temperatures (Fig. 5) are listed. Space charge thicknesses and potentials of samples annealed at 1350 °C (Fig. 6a) and 1500 °C (Fig. 6b) for varying times are summarized in Table 3.

As discussed in section 3.2, space charge thicknesses of GB₂ (90 nm – 100 nm) are thicker than those of GB₁ (60 nm – 70 nm, see Table 1 to Table 3). These values agree with space charge thicknesses typically reported for undoped SrTiO₃ [15,42,66]. The space charge potentials of GB₁ and GB₂ are about 0.15 eV and 0.4 eV, respectively. While GB₂ features space charge potentials comparable to previously reported potentials in SrTiO₃ (0.4 eV to 0.7 eV [74,76]), GB₁ has much lower space charge potential. The space charge thicknesses and potentials of samples annealed in different conditions (Tables 2 and 3) show no clear dependence on annealing time. This would contradict previous prediction that the space charge potential and segregation at GBs changes during microstructure evolution [14]. It should be noted, that samples in this study were not quenched after annealing but cooled at a constant rate of 10 K/min. There would be some time for the GB chemistry to equilibrate again after the annealing step. Samples annealed at the same temperature but for different times would then experience the same temperature curve during cooling which results in similar GB chemistry, i.e., space charge thicknesses or space charge potentials.

In Fig. 7 the specific conductivity and space charge potential of both GB₁ and GB₂ plotted against the annealing temperature are shown. The properties of GB₂ again do not show any clear dependence on the

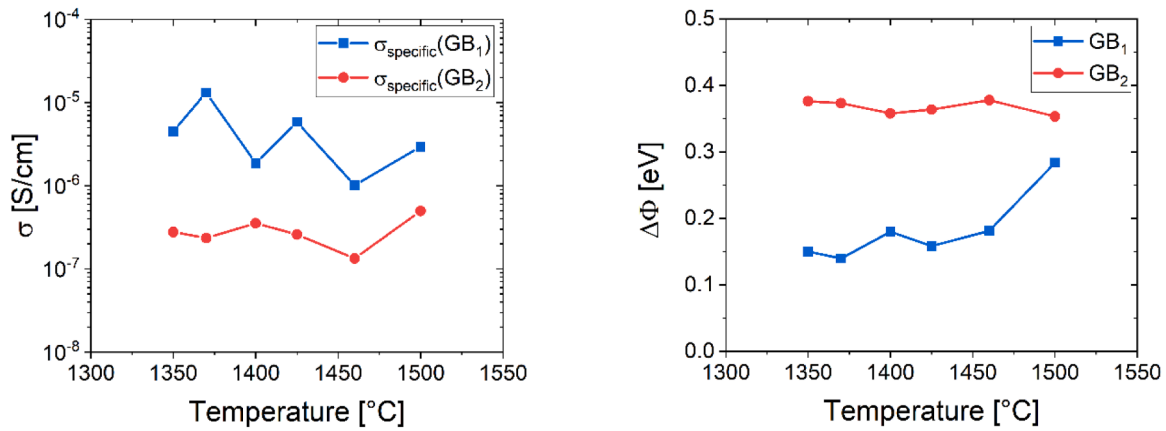


Fig. 7. Dependence of (a) the specific conductivity and (b) the space charge potential of GB₁ and GB₂ on the annealing temperature. Conductivity measurements were all done at 500 °C.

annealing conditions. In the case of GB₁ the data from Table 2 hint on a slight temperature dependence of the properties of GB₁. The specific conductivity of GB₁ tends to decrease with increasing annealing temperature becoming more similar to the specific conductivity of GB₂. The space charge potentials of GB₁ seems to increase with annealing temperature also becoming more similar to that of GB₂.

It is not known if the changes in specific conductivity and space charge potential of GB₁ are due to a change in GB chemistry with GB₁ becoming more and more similar to GB₂ or a change in the ratio between the GB types. The number of GBs and fraction of each type were evaluated but no conclusive dependence on annealing conditions was identified.

It should be noted that space charge thicknesses and potentials of GB₁ and GB₂ should both be interpreted with caution. As mentioned in section 3.2, the nature of the GB impedance signal is not clear and is most likely influenced by current constriction and redirection around highly resistive GBs. Inhomogeneous electric field distribution throughout the sample is expected to further complicate the fitting and evaluation procedure. Accordingly, the data in Tables 2 and 3 contains an unknown error. Furthermore, broad non-Gaussian GB property distributions are sufficient to cause distorted impedance semicircles [79]. Variation of space charge potentials of single GBs in ceramics were already indicated with electron holography. The obtained space charge values also deviated from the average space charge potentials obtained by macroscopic EIS measurements [87]. Within the present study, these issues cannot be clarified; simulations of the impedance responses of mixed conductivity in bimodal microstructures with varying GB properties are necessary.

The last source of error in the evaluation the space charge thickness with the MS model stems from the bulk's mobile defect concentration which has to be calculated based on defect chemistry models. These models again require the samples' acceptor and donor concentration measured by ICP-OES or other suitable methods. In this study, the samples' mobile defect concentration was assumed to be 10^{18} cm^{-3} which is common practice in literature [76] but can introduce additional errors to the evaluation. However, this parameter influences both GB types in the same way and introduce a bias to the results.

3.5. Grain boundary composition

From previous studies, it is known that GBs with different segregation types are present in SrTiO₃ [59,60]. STEM analysis of the chemical composition of GBs in SrTiO₃ based on GB morphologies (faceted, curved, rough or flat) have previously been performed [59,60]. If there are two types of GBs as indicated by the results discussed in section 3.2, GBs with qualitatively varying cationic segregation should be

observable with STEM-EDS.

The GB segregation in undoped SrTiO₃ annealed at 1350 °C for 10 h and 1500 °C for 2 h was investigated in this study. In the case of the sample annealed at 1500 °C for 2 h, a GB between two small grains (S-S), a GB between two large grains (L-L), and a GB between a large and a small grain (L-S) were investigated. The sample annealed at 1350 °C for 10 h features unimodal grain size distribution of only small grains which is why one GB between two small grains was analyzed for this sample. The EDS mappings of those GBs are shown in Fig. 8.

EDS mappings of the GBs reveal clear Sr depletion at all investigated grain boundaries (Fig. 8). In the case of the sample annealed at 1350 °C, Ti segregation was also observed (Fig. 8a). All GBs of the sample annealed at 1500 °C show no Ti segregation at the GB and are comparable in composition (Fig. 8b-d).

In Fig. 9, integrated line scans and the Sr:Ti ratio across the GBs from Fig. 8 are shown. The line-scan of the L-S GB of the sample annealed at 1500 °C (Fig. 9a) shows stronger Sr depletion than the other two GB of the same sample annealed at 1500 °C (Fig. 9 b and Fig. 9 c). The GB of the sample annealed at 1350 °C features Sr depletion similar to that of the L-S GB in the sample annealed at 1500 °C. Additionally, oxygen segregation at the S-S GB (1350 °C) is also observed (Fig. 9 d). Note that the oxygen EDS signal is unreliable due to possible oxygen diffusion during acquisition, and so should not be analyzed quantitatively. The Sr depletion at the GBs becomes more obvious if the Sr:Ti ratios across the GBs is evaluated (Fig. 9 e). The S-S and L-L GB of the sample annealed at 1500 °C have similar compositions with a Sr:Ti ratio of 0.82 and 0.86 respectively. The Sr:Ti ratio of the GB in undoped SrTiO₃ annealed at 1350 °C is around 0.69 and comparable to that of the L-S GB (0.63) in the sample annealed at 1500 °C. Whether the GBs from Fig. 8 and Fig. 9 were Sr deficient / Ti enriched or stoichiometric can be checked using Eq. (1). According to Eq. (1), each GB investigated in the current study is Sr deficient / Ti enriched, yet the degree of Sr deficiency differs between the GBs. A table featuring the results of Equation 1 can be found in the supplementary section (Table S1). Note that the stoichiometry of the GBs can also be investigated using the Gibb'sian GB excess leading to similar results (Table S2). Yet the difference in Sr deficiency or Ti excess might be sufficient to explain the varying space charge potentials. The Sr:Ti ratio in the small and large grain adjacent to the L-S GB in the sample annealed at 1500 °C differs in signal strength (Fig. 9 e). The difference in Sr:Ti is probably caused by channeling effects of different crystal orientation as similar effects are observed in the EDS line-scans (Fig. 9 a).

The varying degrees of Sr depletion at the GBs might be sufficient to explain the distortion of the GB impedance. Still, the presence of two or more GB types with distinct composition (Sr-rich, Ti-rich and stoichiometric) could not be confirmed by STEM-EDS in this study. The

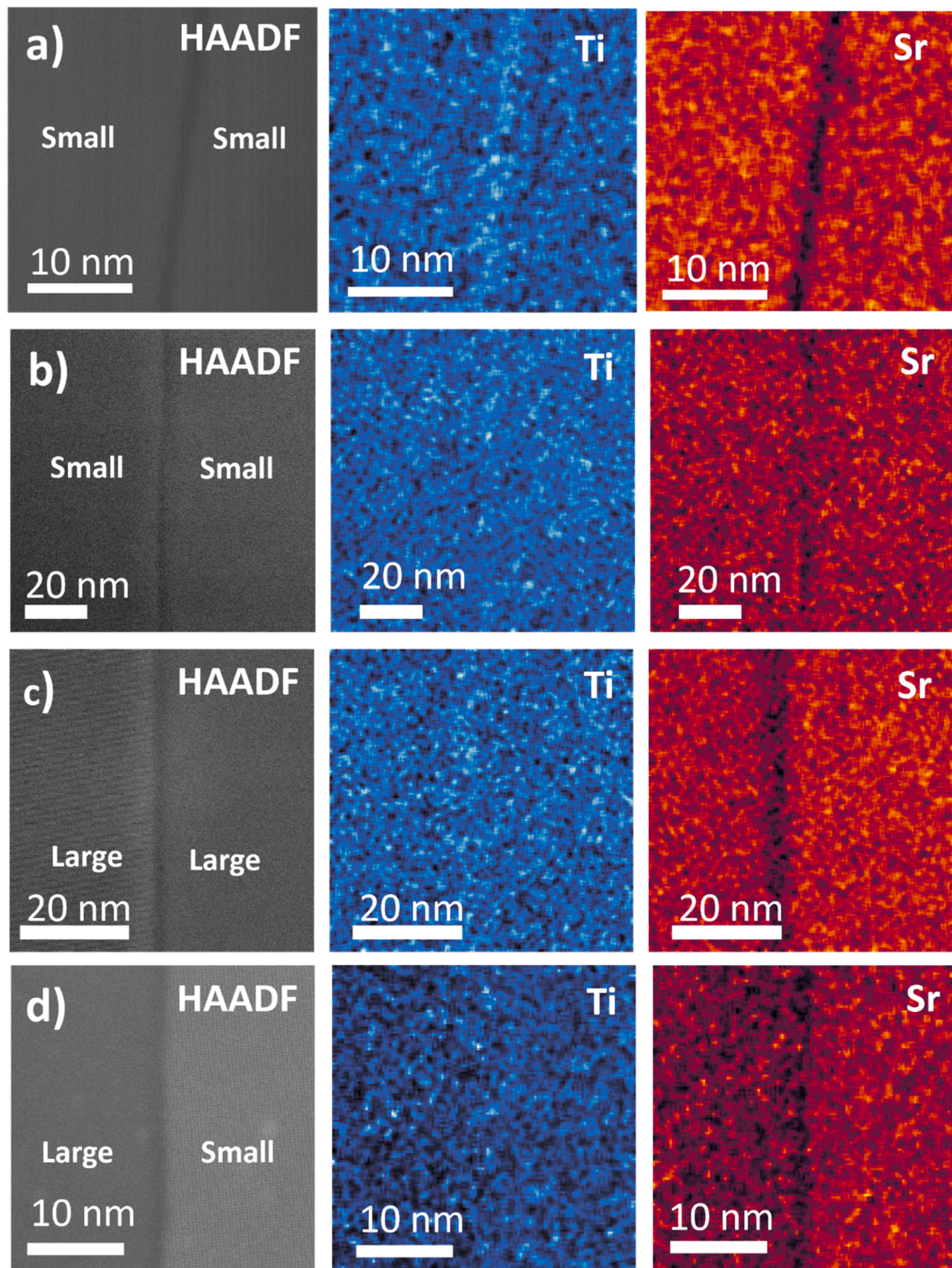


Fig. 8. HAADF images and EDS mapping of Sr and Ti at (a) a GB between two small grains (S-S) in SrTiO_3 annealed at 1350 °C, (b) a GB between two small grains (S-S) in SrTiO_3 annealed at 1500 °C, (c) a GB between two large grains (L-L) in SrTiO_3 annealed at 1500 °C and (d) a GB between a large and a small grain (L-S) in SrTiO_3 annealed at 1500 °C. a) is reprinted, with permission from Elsevier [22].

disagreement on GB chemistry between the current study and literature might be due to the small sample size in this study. The statistical analysis of GB chemistry from literature was re-evaluated and listed in Table 4. GBs were distinguished whether small and/or large grains were adjacent to them instead for their structure. Neither GBs adjacent to

small or large grains had a characteristic GB chemistry, but rather a distribution of composition ranging between Sr-rich, stoichiometric and Ti-rich. GBs adjacent to small grains were statistically more Sr depleted while GBs adjacent to large grains were statistically more stoichiometric. Accordingly, the data in Table 4 (re-evaluated literature data)

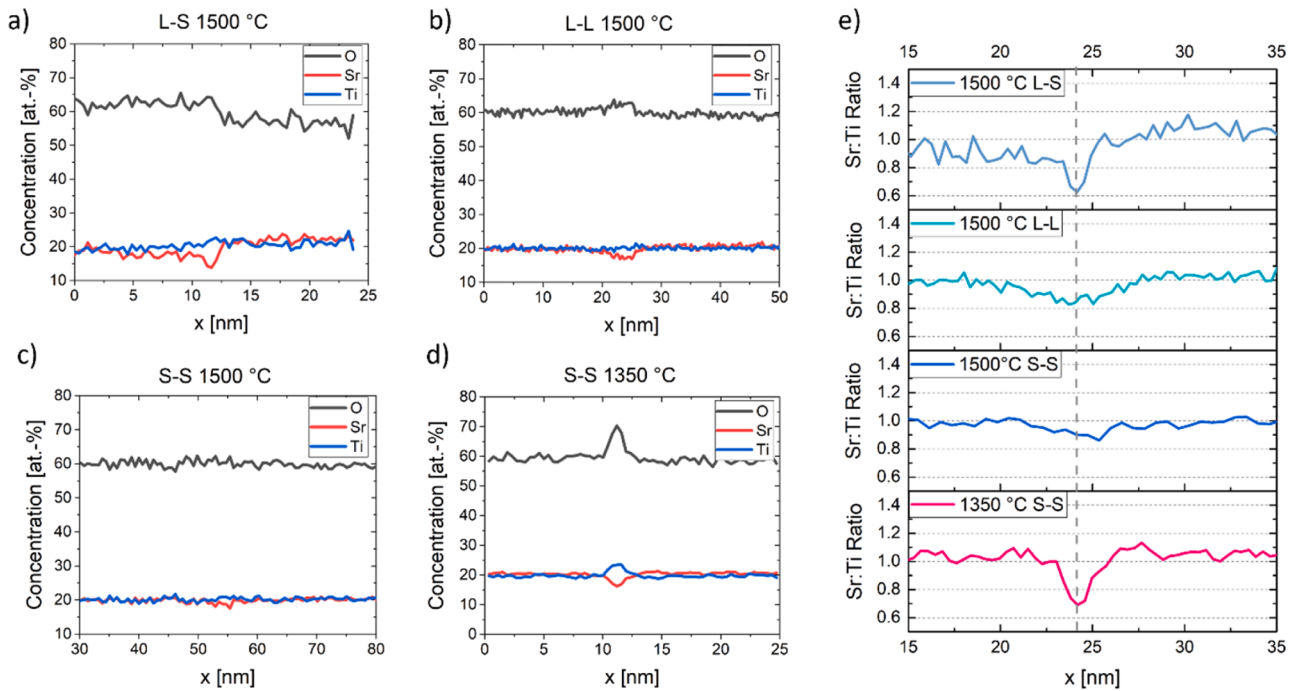


Fig. 9. Integrated linescans of GBs between a) a large and a small grain in a sample annealed at 1500 °C (L-S), b) two large grains in a sample annealed at 1500 °C (L-L), c) two small grains in a sample annealed at 1500 °C (S-S) and d) two small grains in a sample annealed at 1350 °C. The Sr:Ti ratios across the GBs shown in a) to d) are shown in e). d) is reprinted, with permission from Elsevier [22].

Table 4

GB chemistry of GBs adjacent to small and large. GB compositions are differentiated as Sr-rich, neutral and Sr-depleted (Ti-rich). The data featured in this table are re-evaluated data from [60].

GB composition	Small grains (%)	Large grains (%)
Sr-rich	22.5	14.5
neutral	21.1	42.9
Sr-depleted	56.4	42.6

and the data in the current study (Figs. 8 and 9), lead the authors to suspect that there is large variation of GB electrochemistry in undoped SrTiO₃. This variation determines the grain growth behavior. The populations and density of GBs after microstructure evolution of undoped SrTiO₃ then determines the electrochemical response of SrTiO₃ ceramics (Figs. 5–7, Tables 2 and 3).

3.6. Summary and conclusion

Undoped SrTiO₃ ceramic samples were sintered and annealed at different temperature and times. The microstructure of the samples was analyzed using SEM and average grain sizes fit expected values for undoped SrTiO₃. The impact of the annealing conditions on GB properties was analyzed using EIS and STEM-EDS. Impedance spectra of undoped SrTiO₃ show a notably distorted asymmetric GB semicircle which was correlated to the presence of two distinct GB types. The two GB types have different resistivity, space charge layer thicknesses (60 nm to 70 nm and 90 nm to 100 nm) and potentials (0.10 eV to 0.20 eV and 0.35 eV to 0.40 eV). The observation of two GB types in SrTiO₃ agrees with predictions from simulations on microstructure evolution where the presence of two GB types with different GB mobility are likely causing non-Arrhenius grain growth. Due to the lower space charge potential of GB₁ compared to GB₂, GB₁ also have a higher specific conductivity than GB₂ (factor of 3 to 10). The space charge potential of GB₁ approaches values for GB₂ with increasing temperature. The properties of GB₂ are stable over the annealing temperature and the

properties of both GB₁ and GB₂ seem not to change with annealing time. STEM-EDS analysis of GBs revealed the presence of GBs with different magnitudes of Sr depletion in SrTiO₃ which contradicts previous STEM investigation of GB in SrTiO₃ where qualitative differences could be observed. The disagreement is due to the low number of GBs analyzed by STEM-EDS in this study. High $[V_{Sr}^{\bullet}]$ at a S-S GB of the sample annealed at 1350 °C (Sr:Ti=0.69) and a L-S GB of the sample annealed at 1500 °C (Sr:Ti=0.63) were observed (Fig. 9e). S-S and L-L GBs of the sample annealed a 1500 °C have lower $[V_{Sr}^{\bullet}]$ with Sr:Ti ratios of around 0.8. Space charge potentials evaluated from EIS results could not be assigned to either GB composition observed by STEM-EDS.

The current paper investigated the correlation of grain growth, impedance and GB properties of undoped SrTiO₃. The existence of multiple GB types with distinctive properties was indicated by EIS analysis. STEM-EDS analysis also indicates the presence of GB with varying chemistry, yet no conclusive correlation between GB chemistry and GB properties could be made. The possible co-existence of two or more GB types with distinct electrochemistry provides a unique pathway for material design: depending on which GB property distribution is desired; the heating schedule can be chosen which GB type dominates the microstructure evolution and/or the materials electronic properties. This approach can be applied to other functional materials with bimodal microstructure evolution as well. More research is necessary to gain insight on changes in GB chemistry, population and properties with annealing temperature, and their correlation.

CRediT authorship contribution statement

M. Pascal Zahler: Writing – review & editing, Writing – original draft, Project administration, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Dylan Jennings:** Writing – review & editing, Writing – original draft, Validation, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Olivier Guillon:** Validation, Supervision, Resources. **Wolfgang Rheinheimer:** Writing – review & editing, Writing – original draft, Validation, Supervision, Resources, Project administration, Funding acquisition,

Conceptualization.

Declaration of competing interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at [doi:10.1016/j.actamat.2024.120560](https://doi.org/10.1016/j.actamat.2024.120560).

References

- [1] H. Yokokawa, N. Sakai, T. Horita, K. Yamaji, M.E. Brito, Electrolytes for solid-oxide fuel cells, *MRS Bull.* 30 (2005) 591–595, <https://doi.org/10.1557/mrs2005.166>.
- [2] J.W. Fergus, Electrolytes for solid oxide fuel cells, *J. Power Sources* 162 (2006) 30–40, <https://doi.org/10.1016/j.jpowsour.2006.06.062>.
- [3] F. Tietz, Materials selection for solid oxide fuel cells, *MSF* 426–432 (2003) 4465–4470, <https://doi.org/10.4028/www.scientific.net/MSF.426-432.4465>.
- [4] S. Dwivedi, Solid oxide fuel cell: materials for anode, cathode and electrolyte, *Int. J. Hydrogen Energy* 45 (2020) 23988–24013, <https://doi.org/10.1016/j.ijhydene.2019.11.234>.
- [5] H. Shi, C. Su, R. Ran, J. Cao, Z. Shao, Electrolyte materials for intermediate-temperature solid oxide fuel cells, *Progr. Natural Sci. Mater. Int.* 30 (2020) 764–774, <https://doi.org/10.1016/j.pnsc.2020.09.003>.
- [6] X. Yao, B. Huang, J. Yin, G. Peng, Z. Huang, C. Gao, D. Liu, X. Xu, All-solid-state lithium batteries with inorganic solid electrolytes: review of fundamental science, *Chinese Phys. B* 25 (2016) 018802, <https://doi.org/10.1088/1674-1056/25/1/018802>.
- [7] M.V. Reddy, C.M. Julien, A. Mauger, K. Zaghib, Sulfide and oxide inorganic solid electrolytes for all-solid-state Li batteries: a review, *Nanomaterials* 10 (2020) 1606, <https://doi.org/10.3390/nano10081606>.
- [8] J.G. Kim, B. Son, S. Mukherjee, N. Schuppert, A. Bates, O. Kwon, M.J. Choi, H. Y. Chung, S. Park, A review of lithium and non-lithium based solid state batteries, *J. Power Sources* 282 (2015) 299–322, <https://doi.org/10.1016/j.jpowsour.2015.02.054>.
- [9] J. Maier, Ionic conduction in space charge regions, *Progress in Solid State Chemistry* 23 (1995) 171–263, [https://doi.org/10.1016/0079-6786\(95\)00004-E](https://doi.org/10.1016/0079-6786(95)00004-E).
- [10] A. Tschöpe, S. Kilassonia, R. Birringer, The grain boundary effect in heavily doped cerium oxide, *Solid. State Ion.* 173 (2004) 57–61, <https://doi.org/10.1016/j.ssi.2004.07.052>.
- [11] A. Tschöpe, Interface defect chemistry and effective conductivity in polycrystalline cerium oxide, *J. Electroceram.* 14 (2005) 5–23, <https://doi.org/10.1007/s10832-005-6580-6>.
- [12] R. Hagenbeck, R. Waser, Influence of temperature and interface charge on the grain-boundary conductivity in acceptor-doped SrTiO₃ ceramics, *J. Appl. Phys.* 83 (1998) 2083–2092, <https://doi.org/10.1063/1.366941>.
- [13] X. Guo, Physical origin of the intrinsic grain-boundary resistivity of stabilized-zirconia: role of the space-charge layers, *Solid. State Ion.* 81 (1995) 235–242, [https://doi.org/10.1016/0167-2738\(95\)00180-E](https://doi.org/10.1016/0167-2738(95)00180-E).
- [14] K.S.N. Vikrant, W. Rheinheimer, R.E. García, Electrochemical drag effect on grain boundary motion in ionic ceramics, *NPJ. Comput. Mater.* 6 (2020) 165, <https://doi.org/10.1038/s41524-020-00418-z>.
- [15] G. Gregori, R. Merkle, J. Maier, Ion conduction and redistribution at grain boundaries in oxide systems, *Prog. Mater. Sci.* 89 (2017) 252–305, <https://doi.org/10.1016/j.pmatsci.2017.04.009>.
- [16] R. Waser, R. Hagenbeck, Grain boundaries in dielectric and mixed-conducting ceramics, *Acta Mater.* 48 (2000) 797–825, [https://doi.org/10.1016/S1359-6454\(99\)00367-5](https://doi.org/10.1016/S1359-6454(99)00367-5).
- [17] W. Rheinheimer, J.P. Parras, J. Preusker, R.A. De Souza, M.J. Hoffmann, Grain growth in strontium titanate in electric fields: the impact of space-charge on the grain-boundary mobility, *J. Am. Ceram. Soc.* 102 (2019) 3779–3790, <https://doi.org/10.1111/jace.16217>.
- [18] F. Gunkel, R. Waser, A.H.H. Ramadan, R.A. De Souza, S. Hoffmann-Eifert, R. Dittmann, Space charges and defect concentration profiles at complex oxide interfaces, *Phys. Rev. B* 93 (2016) 245431, <https://doi.org/10.1103/PhysRevB.93.245431>.
- [19] R.A. De Souza, The formation of equilibrium space-charge zones at grain boundaries in the perovskite oxide SrTiO₃, *Phys. Chem. Chem. Phys.* 11 (2009) 9939, <https://doi.org/10.1039/b904100a>.
- [20] R. Hagenbeck, R. Waser, Detailed temperature dependence of the space charge layer width at grain boundaries in acceptor-doped SrTiO₃-ceramics, *J. Eur. Ceram. Soc.* 19 (1999) 683–686, [https://doi.org/10.1016/S0955-2219\(98\)00296-9](https://doi.org/10.1016/S0955-2219(98)00296-9).
- [21] D.S. Mebane, R.A. De Souza, A generalised space-charge theory for extended defects in oxygen-ion conducting electrolytes: from dilute to concentrated solid solutions, *Energy Environ. Sci.* 8 (2015) 2935–2940, <https://doi.org/10.1039/C5EE02060C>.
- [22] M.P. Zahler, D. Jennings, M. Kindelmann, O. Guillon, W. Rheinheimer, Reactive FAST/SPS sintering of strontium titanate as a tool for grain boundary engineering, *J. Eur. Ceram. Soc.* 43 (2023) 6925–6933, <https://doi.org/10.1016/j.jeurceramsoc.2023.07.021>.
- [23] J.W. Cahn, The impurity-drag effect in grain boundary motion, *Acta Metall.* 10 (1962) 789–798, [https://doi.org/10.1016/0001-6160\(62\)90092-5](https://doi.org/10.1016/0001-6160(62)90092-5).
- [24] W. Rheinheimer, M. Bäurer, C.A. Handwerker, J.E. Blendell, M.J. Hoffmann, Growth of single crystalline seeds into polycrystalline strontium titanate: anisotropy of the mobility, intrinsic drag effects and kinetic shape of grain boundaries, *Acta Mater.* 95 (2015) 111–123, <https://doi.org/10.1016/j.actamat.2015.05.019>.
- [25] M. Hillert, Solute drag, solute trapping and diffusional dissipation of Gibbs energy, *Acta Mater.* 47 (1999) 4481–4505, [https://doi.org/10.1016/S1359-6454\(99\)00336-5](https://doi.org/10.1016/S1359-6454(99)00336-5).
- [26] R. Kirchheim, Reducing grain boundary, dislocation line and vacancy formation energies by solute segregation. I. Theoretical background, *Acta Mater.* 55 (2007) 5129–5138, <https://doi.org/10.1016/j.actamat.2007.05.047>.
- [27] R. Kirchheim, Reducing grain boundary, dislocation line and vacancy formation energies by solute segregation. II. Experimental evidence and consequences, *Acta Mater.* 55 (2007) 5139–5148, <https://doi.org/10.1016/j.actamat.2007.05.033>.
- [28] S.G. Kim, Y.B. Park, Grain boundary segregation, solute drag and abnormal grain growth, *Acta Mater.* 56 (2008) 3739–3753, <https://doi.org/10.1016/j.actamat.2008.04.007>.
- [29] F. Abdeljawad, P. Lu, N. Argibay, B.G. Clark, B.L. Boyce, S.M. Foiles, Grain boundary segregation in immiscible nanocrystalline alloys, *Acta Mater.* 126 (2017) 528–539, <https://doi.org/10.1016/j.actamat.2016.12.036>.
- [30] M.N. Rahaman, R. Manalart, Grain boundary mobility of BaTiO₃ doped with aliovalent cations, *J. Eur. Ceram. Soc.* 18 (1998) 1063–1071, [https://doi.org/10.1016/S0955-2219\(97\)00215-X](https://doi.org/10.1016/S0955-2219(97)00215-X).
- [31] K.S.N. Vikrant, W. Rheinheimer, H. Sternlicht, M. Bäurer, R.E. García, Electrochemically-driven abnormal grain growth in ionic ceramics, *Acta Mater.* 200 (2020) 727–734, <https://doi.org/10.1016/j.actamat.2020.08.027>.
- [32] W. Rheinheimer, E. Schoof, M. Selzer, B. Nestler, M.J. Hoffmann, Non-Arrhenius grain growth in strontium titanate: quantification of bimodal grain growth, *Acta Mater.* 174 (2019) 105–115, <https://doi.org/10.1016/j.actamat.2019.05.040>.
- [33] W. Rheinheimer, M.J. Hoffmann, Grain growth in perovskites: what is the impact of boundary transitions? *Curr. Opin. Solid. State Mater. Sci.* 20 (2016) 286–298, <https://doi.org/10.1016/j.cossms.2016.04.004>.
- [34] S.-J.L. Kang, S.-Y. Ko, S.-Y. Moon, Mixed control of boundary migration and the principle of microstructural evolution, *J. Ceram. Soc. Jap.* 124 (2016) 259–267, <https://doi.org/10.2109/jcersj2.15262>.
- [35] G.S. Rohrer, Influence of interface anisotropy on grain growth and coarsening, *Annu. Rev. Mater. Res.* 35 (2005) 99–126, <https://doi.org/10.1146/annurev.matsci.33.041002.094657>.
- [36] G.S. Rohrer, Grain boundary energy anisotropy: a review, *J. Mater. Sci.* 46 (2011) 5881–5895, <https://doi.org/10.1007/s10853-011-5677-3>.
- [37] A. Subramaniam, C.T. Koch, R.M. Cannon, M. Rühle, Intergranular glassy films: an overview, *Mater. Sci. Eng. A* 422 (2006) 3–18, <https://doi.org/10.1016/j.msea.2006.01.004>.
- [38] S.-Y. Choi, D.-Y. Yoon, S.-J.L. Kang, Kinetic formation and thickening of intergranular amorphous films at grain boundaries in barium titanate, *Acta Mater.* 52 (2004) 3721–3726, <https://doi.org/10.1016/j.actamat.2004.04.026>.
- [39] J.W. Cahn, Critical point wetting, *J. Chem. Phys.* 66 (1977) 3667–3672, <https://doi.org/10.1063/1.434402>.
- [40] S.J. Dillon, M. Tang, W.C. Carter, M.P. Harmer, Complexion: a new concept for kinetic engineering in materials science, *Acta Mater.* 55 (2007) 6208–6218, <https://doi.org/10.1016/j.actamat.2007.07.029>.
- [41] P.R. Cantwell, M. Tang, S.J. Dillon, J. Luo, G.S. Rohrer, M.P. Harmer, Grain boundary complexions, *Acta Mater.* 62 (2014) 1–48, <https://doi.org/10.1016/j.actamat.2013.07.037>.
- [42] S.K. Rout, J. Bera, Grain and grain-boundary study of acceptor doped SrTiO₃ ceramics using impedance spectroscopy, *Ferroelectrics* 323 (2005) 79–84, <https://doi.org/10.1080/00150190500308777>.
- [43] B.-K. Lee, S.-Y. Chung, S.-J.L. Kang, Grain boundary faceting and abnormal grain growth in BaTiO₃, *Acta Mater.* 48 (2000) 1575–1580, [https://doi.org/10.1016/S1359-6454\(99\)00434-6](https://doi.org/10.1016/S1359-6454(99)00434-6).
- [44] S.-M. An, S.-J.L. Kang, Boundary structural transition and grain growth behavior in BaTiO₃ with Nd₂O₃ doping and oxygen partial pressure change, *Acta Mater.* 59 (2011) 1964–1973, <https://doi.org/10.1016/j.actamat.2010.11.062>.
- [45] W. Rheinheimer, M.J. Hoffmann, Grain growth transitions of perovskite ceramics and their relationship to abnormal grain growth and bimodal microstructures, *J. Mater. Sci.* 51 (2016) 1756–1765, <https://doi.org/10.1007/s10853-015-9535-6>.
- [46] K. Kim, W. Jo, H. Jin, N. Hwang, D. Kim, Abnormal grain growth of lead zirconium titanate (PZT) ceramics induced by the penetration twin, *J. Am. Ceram. Soc.* 89 (2006) 1530–1533, <https://doi.org/10.1111/j.1551-2916.2006.00934.x>.

- [47] M. Li, M.J. Pietrowski, R.A. De Souza, H. Zhang, I.M. Reaney, S.N. Cook, J. A. Kilner, D.C. Sinclair, A family of oxide ion conductors based on the ferroelectric perovskite $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$, *Nature Mater* 13 (2014) 31–35, <https://doi.org/10.1038/nmat3782>.
- [48] J.G. Fisher, S.-J.L. Kang, Microstructural changes in $(\text{K}_{0.5}\text{Na}_{0.5})\text{NbO}_3$ ceramics sintered in various atmospheres, *J. Eur. Ceram. Soc.* 29 (2009) 2581–2588, <https://doi.org/10.1016/j.jeurceramsoc.2009.02.006>.
- [49] G. Han, J. Ryu, C. Ahn, W. Yoon, J. Choi, B. Hahn, J. Kim, J. Choi, D. Park, High piezoelectric properties of KNN-based thick films with abnormal grain growth, *J. Am. Ceram. Soc.* 95 (2012) 1489–1492, <https://doi.org/10.1111/j.1551-2916.2012.05139.x>.
- [50] C.-W. Ahn, A. Rahman, J. Ryu, J.-J. Choi, J.-W. Kim, W.-H. Yoon, J.-H. Choi, D.-S. Park, B.-D. Hahn, Composition design for growth of single crystal by abnormal grain growth in modified potassium sodium niobate ceramics, *Cryst. Growth Des.* 16 (2016) 6586–6592, <https://doi.org/10.1021/acs.cgd.6b01287>.
- [51] K. Jiang, L. Zhang, B. Li, P. Li, S. Yu, R. Sun, Z. Fu, X. Cao, Importance of uniformity of grain size to reduce dc degradation and improve reliability of ultra-thin BaTiO_3 -based MLCCs, *Ceram. Int.* 48 (2022) 30020–30030, <https://doi.org/10.1016/j.ceramint.2022.06.271>.
- [52] W. Rheinheimer, M.J. Hoffmann, Non-Arrhenius behavior of grain growth in strontium titanate: new evidence for a structural transition of grain boundaries, *Scr Mater.* 101 (2015) 68–71, <https://doi.org/10.1016/j.scriptamat.2015.01.021>.
- [53] M.N. Kelly, W. Rheinheimer, M.J. Hoffmann, G.S. Rohrer, Anti-thermal grain growth in SrTiO_3 : coupled reduction of the grain boundary energy and grain growth rate constant, *Acta Mater.* 149 (2018) 11–18, <https://doi.org/10.1016/j.actamat.2018.02.030>.
- [54] J.E. Burke, D. Turnbull, Recrystallization and grain growth, *Progr. Metal Phys.* 3 (1952) 220–292, [https://doi.org/10.1016/0502-8205\(52\)90009-9](https://doi.org/10.1016/0502-8205(52)90009-9).
- [55] M. Hillert, On the theory of normal and abnormal grain growth, *Acta Metall.* 13 (1965) 227–238, [https://doi.org/10.1016/0001-6160\(65\)90200-2](https://doi.org/10.1016/0001-6160(65)90200-2).
- [56] K. Lücke, K. Detert, A quantitative theory of grain-boundary motion and recrystallization in metals in the presence of impurities, *Acta Metall.* 5 (1957) 628–637, [https://doi.org/10.1016/0001-6160\(57\)90109-8](https://doi.org/10.1016/0001-6160(57)90109-8).
- [57] D. Fan, S.P. Chen, L.-Q. Chen, Computer simulation of grain growth kinetics with solute drag, *J. Mater. Res.* 14 (1999) 1113–1123, <https://doi.org/10.1557/JMR.1999.0147>.
- [58] F. Liu, R. Kirchheim, Grain boundary saturation and grain growth, *Scr. Mater.* 51 (2004) 521–525, <https://doi.org/10.1016/j.scriptamat.2004.05.042>.
- [59] S.-J. Shih, S. Lozano-Perez, D.J.H. Cockayne, Investigation of grain boundaries for abnormal grain growth in polycrystalline SrTiO_3 , *J. Mater. Res.* 25 (2010) 260–265, <https://doi.org/10.1557/JMR.2010.0046>.
- [60] M. Bäurer, S.-J. Shih, C. Bishop, M.P. Harmer, D. Cockayne, M.J. Hoffmann, Abnormal grain growth in undoped strontium and barium titanate, *Acta Mater.* 58 (2010) 290–300, <https://doi.org/10.1016/j.actamat.2009.09.007>.
- [61] F. De La Peña, E. Prestat, V.T. Fauske, P. Burdet, J. Lähnemann, P. Jokubauskas, T. Furnival, M. Nord, T. Ostasevicius, K.E. MacArthur, D.N. Johnstone, M. Sarahan, J. Taillon, T. Aarholt, P. Quinn-Dls, V. Migunov, A. Eljarrat, J. Caron, C. Francis, T. Nemoto, T. Poon, S. Mazzucco, Actions-User, N. Tappy, N. Cautelaerts, Suhas Somnath, T. Slater, M. Walls, F. Winkler, H.W. Ånes, hyperspy/hyperspy: release v1.7.3, (2022). [10.5281/ZENODO.592838](https://doi.org/10.5281/ZENODO.592838).
- [62] J.E. Bauerle, Study of solid electrolyte polarization by a complex admittance method, *J. Phys. Chem. Solids* 30 (1969) 2657–2670, [https://doi.org/10.1016/0022-3697\(69\)90039-0](https://doi.org/10.1016/0022-3697(69)90039-0).
- [63] J. Jamnik, Impedance spectroscopy of mixed conductors with semi-blocking boundaries, *Solid. State Ion.* 157 (2003) 19–28, [https://doi.org/10.1016/S0167-2738\(02\)00183-2](https://doi.org/10.1016/S0167-2738(02)00183-2).
- [64] J. Jamnik, J. Maier, Generalised equivalent circuits for mass and charge transport: chemical capacitance and its implications, *Phys. Chem. Chem. Phys.* 3 (2001) 1668–1678, <https://doi.org/10.1039/b100180i>.
- [65] J. Jamnik, J. Maier, S. Pejovnik, A powerful electrical network model for the impedance of mixed conductors, *Electrochim. Acta* 44 (1999) 4139–4145, [https://doi.org/10.1016/S0013-4686\(99\)00128-0](https://doi.org/10.1016/S0013-4686(99)00128-0).
- [66] I. Denk, J. Claus, J. Maier, Electrochemical Investigations of SrTiO_3 Boundaries, *J. Electrochem. Soc.* 144 (1997) 3526–3536, <https://doi.org/10.1149/1.1838044>.
- [67] X. Guo, J. Fleig, J. Maier, Separation of electronic and ionic contributions to the grain boundary conductivity in acceptor-doped SrTiO_3 , *J. Electrochem. Soc.* 148 (2001) J50, <https://doi.org/10.1149/1.1389344>.
- [68] M. Vollmann, R. Waser, Grain boundary defect chemistry of acceptor-doped titanates: space charge layer width, *J. Am. Ceram. Soc.* 77 (1994) 235–243, <https://doi.org/10.1111/j.1151-2916.1994.tb06983.x>.
- [69] S.M. Haile, D.L. West, J. Campbell, The role of microstructure and processing on the proton conducting properties of gadolinium-doped barium cerate, *J. Mater. Res.* 13 (1998) 1576–1595, <https://doi.org/10.1557/JMR.1998.0219>.
- [70] T. Van Dijk, A.J. Burggraaf, Grain boundary effects on ionic conductivity in ceramic $\text{Gd}_{x}\text{Zr}_{1-x}\text{O}_{2-(x/2)}$ solid solutions, *Phys. Stat. Sol.* 63 (1981) 229–240, <https://doi.org/10.1002/pssa.2210630131>.
- [71] J.C.C. Abrantes, J.A. Labrincha, J.R. Frade, Applicability of the brick layer model to describe the grain boundary properties of strontium titanate ceramics, *J. Eur. Ceram. Soc.* 20 (2000) 1603–1609, [https://doi.org/10.1016/S0955-2219\(00\)00022-4](https://doi.org/10.1016/S0955-2219(00)00022-4).
- [72] P. Balaya, J. Jamnik, J. Fleig, J. Maier, Mesoscopic electrical conduction in nanocrystalline SrTiO_3 , *Appl. Phys. Lett.* 88 (2006) 062109, <https://doi.org/10.1063/1.2171798>.
- [73] J. Fleig, S. Rodewald, J. Maier, Microcontact impedance measurements of individual highly resistive grain boundaries: general aspects and application to acceptor-doped SrTiO_3 , *J. Appl. Phys.* 87 (2000) 2372–2381, <https://doi.org/10.1063/1.372189>.
- [74] J. Fleig, The grain boundary impedance of random microstructures: numerical simulations and implications for the analysis of experimental data, *Solid. State Ion.* 150 (2002) 181–193, [https://doi.org/10.1016/S0167-2738\(02\)00274-6](https://doi.org/10.1016/S0167-2738(02)00274-6).
- [75] P. Debye, E. Hückel, Zur Theorie der Elektrolyte. I. Gefrierpunktserniedrigung und verwandte Erscheinungen, *Physikalische Zeitschrift* 24 (1923) 305.
- [76] R.A.D. Souza, J. Fleig, R. Merkle, J. Maier, SrTiO_3 : a model electroceramic, *Int. J. Mater. Res.* 94 (2003) 218–225, <https://doi.org/10.3139/ijmr-2003-0043>.
- [77] M. Vollmann, R. Hagenbeck, R. Waser, Grain-boundary defect chemistry of acceptor-doped titanates: inversion layer and low-field conduction, *J. Am. Ceram. Soc.* 80 (1997) 2301–2314, <https://doi.org/10.1111/j.1151-2916.1997.tb03121.x>.
- [78] M. Bäurer, L.F. Zagonel, N. Barrett, M.J. Hoffmann, Changes in macroscopic behaviour through segregation in niobium doped strontium titanate, *J. Phys.: Conf. Ser.* 94 (2008) 012015, <https://doi.org/10.1088/1742-6596/94/1/012015>.
- [79] J. Fleig, J. Maier, The impedance of ceramics with highly resistive grain boundaries: validity and limits of the brick layer model, *J. Eur. Ceram. Soc.* 19 (1999) 693–696, [https://doi.org/10.1016/S0955-2219\(98\)00298-2](https://doi.org/10.1016/S0955-2219(98)00298-2).
- [80] J. Fleig, The influence of non-ideal microstructures on the analysis of grain boundary impedances, *Solid. State Ion.* 131 (2000) 117–127, [https://doi.org/10.1016/S0167-2738\(00\)00627-5](https://doi.org/10.1016/S0167-2738(00)00627-5).
- [81] S. Rodewald, J. Fleig, J. Maier, Microcontact impedance spectroscopy at single grain boundaries in Fe-Doped SrTiO_3 polycrystals, *J. Am. Ceram. Soc.* 84 (2001) 521–530, <https://doi.org/10.1111/j.1151-2916.2001.tb00693.x>.
- [82] J. Fleig, J. Maier, A finite element study on the grain boundary impedance of different microstructures, *J. Electrochem. Soc.* 145 (1998) 2081–2089, <https://doi.org/10.1149/1.1838600>.
- [83] R.A. De Souza, Oxygen diffusion in SrTiO_3 and related perovskite oxides, *Adv. Funct. Mater.* 25 (2015) 6326–6342, <https://doi.org/10.1002/adfm.201500827>.
- [84] R.A. Maier, C.A. Randall, Low-temperature ionic conductivity of an acceptor-doped perovskite: I. Impedance of single-crystal SrTiO_3 , *J. Am. Ceram. Soc.* 99 (2016) 3350–3359, <https://doi.org/10.1111/jace.14348>.
- [85] R. Moos, K.H. Haerdtl, Defect chemistry of donor-doped and undoped strontium titanate ceramics between 1000° and 1400°C, *J. Am. Ceram. Soc.* 80 (2005) 2549–2562, <https://doi.org/10.1111/j.1151-2916.1997.tb03157.x>.
- [86] J.N. Baker, P.C. Bowes, D.M. Long, A. Muballeghe, J.S. Harris, E.C. Dickey, D. L. Irving, Defect mechanisms of coloration in Fe-doped SrTiO_3 from first principles, *Appl. Phys. Lett.* 110 (2017) 122903, <https://doi.org/10.1063/1.4978861>.
- [87] X. Xu, Y. Liu, J. Wang, D. Isheim, V.P. Dravid, C. Phatak, S.M. Haile, Variability and origins of grain boundary electric potential detected by electron holography and atom-probe tomography, *Nat. Mater.* 19 (2020) 887–893, <https://doi.org/10.1038/s41563-020-0656-1>.