Grain growth in perovskites: What is the impact of boundary transitions?

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Abstract
Several perovskite ceramics are known to have non-Arrhenius type grain growth. The growth transitions are coupled to bimodal microstructures and seem to be caused by the existence, coexistence and transition of two different grain boundary types. This paper gives a review on the details of the grain growth transitions in perovskite ceramics. A simple mean field approach and standard grain growth experiments are used. However, this approach is far too simple to understand bimodal anisotropic grain growth completely as apparent in perovskites. Important parameters such as atomistic boundary structure, segregation effects, wetting transitions, faceting, grain boundary stoichiometry, space charge and interfacial drag effects are discussed with respect to their impact on grain growth in perovskites. A summary of open questions and future directions is given.

Keywords
Grain growth; perovskites; complexions; grain growth transition; bimodal grain growth; anisotropy, grain growth stagnation

1. Introduction

Perovskite-type materials are widely used in electronic systems such as sensors, actuators, capacitors and ionic conductors. In this wide field of applications macroscopic materials properties strongly depend on microstructural evolution and on the behavior of interfaces during processing.

As can been seen in the materials science literature, changes in interfacial properties are being related to a multitude of different factors, including transitions in grain boundary structure and mobility as a function of temperature, misorientation, boundary plane and composition as well as coupled grain boundary migration and stress generation. In alumina, for example, adsorption (complexion) transitions of the grain boundaries with dopant composition were shown to change the grain boundary mobility and thereby the local grain growth rate by several orders of magnitude [1, 2]. These grain boundary states are thermodynamically stable and exist at temperatures below the wetting transition of grain boundaries and can be interpreted as grain boundary phases [3, 4]. These complexions have a strong impact on microstructural evolution and can result in strong bimodal grain growth. In sintering these transitions can be used to optimize the shrinkage behavior [5-7].

Few studies investigated the relationship between boundary type or complexion and microstructural evolution. Nevertheless several grain growth transitions were reported with grain growth rates indicating non-Arrhenius type behavior [8-12]. For example strontium titanate shows strongly decreasing grain growth rates with increasing temperatures

between 1350°C and 1425°C; outside of this temperature range standard Arrhenius type behavior can be observed [8, 10, 11]. Within the transition, bimodal microstructures appear. Numerous cases of bimodal grain growth in perovskite ceramics are known without thorough knowledge of the grain growth behavior, e.g. KNN (Sodium Potassium Niobate [13-16]), NBT-BT (Sodium Bismuth Barium Titanate [17, 18]) and PMN-PT (Lead Magnesium Niobate-Lead Titanate [19, 20]). Sometimes this effect can be used to grow single crystals from polycrystals [20]. Thus the existence of grain growth transitions seems to be a general feature of perovskite ceramics. However, the details of the growth transitions are not clear in all cases; further investigation is needed to answer open questions and to use the growth effects to tailor microstructures for different applications.

This paper gives a review on grain growth transitions and their relationship to interfacial properties in perovskite ceramics. Macroscopic mean field modelling allows quantifying the general impact on microstructural evolution. The bimodal appearance of microstructure allows correlating the transitions to the coexistence and transition of two boundary types. Different factors from atomistic structure, grain boundary faceting, anisotropy and wetting transitions to boundary stoichiometry and space charge were found to be relevant for the grain growth transitions of perovskite ceramics. The focus of this review is on strontium titanate, but related information on other materials (e.g. barium titanate) is included as well.

2. Grain growth transitions in perovskites

2.1. Grain growth and mean field modelling

Several different geometric approaches to grain growth were used to describe grain growth in a mean field. The most common approach gives the evolution of the mean grain size as [21-23]

$$r^2 - r_0^2 = \frac{1}{4}kt \qquad 1$$

with r as mean grain radius, r_0 as initial mean grain radius at time $t = 0$, $k = 2\alpha\gamma m$ as grain growth rate with $\alpha \approx 1$ as a geometric constant, γ as grain boundary energy and m as grain boundary mobility. The grain growth rate k provides a simple measure to characterize overall grain growth and is easily obtained by standard grain growth experiments.

Grain growth is a thermally activated process; thus k usually shows Arrhenius type behavior. However, several materials are known to show non-Arrhenius grain growth with transitions of the grain growth rate, e.g. doped alumina [1, 2].

In contrast to alumina, several grain growth transitions are known in high purity perovskites free from any dopants. Most data is available for the perovskite model system strontium titanate: A grain growth transition was found between 1350°C and 1425°C in oxidizing atmosphere ([8-10], Fig. 1a). A gradual decrease of k by two orders of magnitude with increasing temperature occurs. In and above the transition regime microstructures indicate bimodal grain size distributions with an increasing fraction of large grains with rising temperature [10, 11]. In reducing atmosphere, a similar grain growth transition was found between 1350°C and 1400°C ([24], Fig. 1c), but additionally a second transition appears

between 1460°C and 1500°C. The second transition results in higher growth rates and is again coupled with bimodal microstructures (Fig. 1d).

Another grain growth transition was found in barium titanate ([12], Fig. 1e). Again a gradual behavior of k with bimodal microstructures is observed within the transition regime (Fig. 1f). In strontium titanate the activation energy for grain growth did not change with the growth transition, whereas it increases in barium titanate above the growth transition.

Finally, in lithium lanthanum titanate (LLTO) a grain growth transition to lower grain growth rates exists at 1400°C as shown in Fig. 1g [11]. Below 1400°C, classical Arrhenius-type behavior is observed. As for strontium and barium titanate, the transition regime is characterized by bimodal microstructures (Fig. 1h).

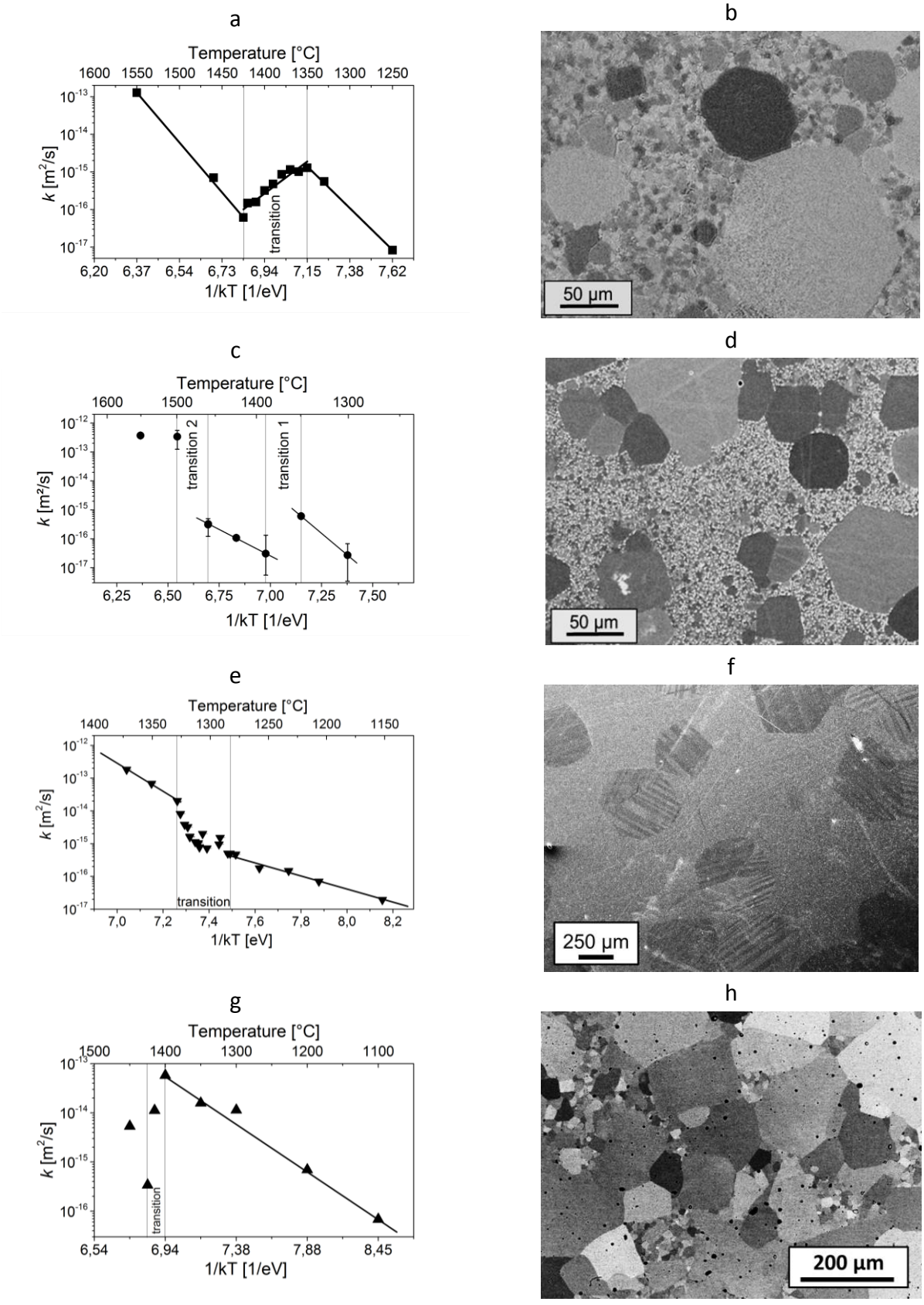

Figure 1: Arrhenius graphs for strontium titanate in oxidizing (a) and reducing atmosphere (c), barium titanate (e) and lithium lanthanum titanate (LLTO, g). In all four cases one or two grain growth transitions were found. Above the transition temperatures bimodal microstructures appear for strontium titanate in oxidizing (b) and reducing atmosphere (d), barium titanate (f) and LLTO (h) [10-12, 24].

2.2. **Bimodal microstructures in the grain growth transition of strontium titanate**

For all grain growth transitions discussed in the previous section, bimodal grain growth is apparent. Two recent studies focused on the bimodality of microstructures in strontium titanate [10, 11]: Fig. 2 shows microstructures after 10h at 1350°C (a, below the grain growth transition), 1390°C and 1400°C (b and c, both in the transition range) and 1425°C (d, above the transition) and the corresponding grain size distributions (e). While at 1350°C the microstructure is unimodal [10], with increasing temperatures an increasing fraction of small grains appears in the microstructures. At 1425°C, very few large grains remain in the microstructure. This trend is quantified in the grain size distributions in Fig. 2f.

According to this microstructural appearance, the existence and coexistence of two grain boundary types seems reasonable: The growth of large grains is dominated by a high mobility boundary type (donated as type 1), while small grains are correlated to a low mobility boundary type (donated as type 2). Within the grain growth transition, the area fraction of the two boundary types changes: below 1350°C, the microstructural evolution is dominated by type 1 boundaries. The fraction of small grains appearing in the microstructures with increasing temperatures is caused by an increasing fraction of type 2 boundaries. Accordingly, the grain growth transition is effectively a grain boundary transition. This behavior seems to apply for barium titanate and LLTO as well [11]. While parts of this behavior are very similar e.g. to alumina [1] or yttria [25], the gradual transition of microstructural appearance and grain size distributions seems to be unique in perovskites.

The grain growth transition can only base on a grain boundary transition, if the grain boundary type is consistent during growth: a high mobility (or a low mobility) boundary needs to continue growing at high (or low) mobility to cause bimodal grain growth. The growth of single crystalline seeds in barium and strontium titanate provides experimental evidence for this assumption [26-28]; similar findings were published for alumina as well [29-31].

The bimodal microstructures suggest that the grain boundary transition occurs for the complete grains. However, this is most likely not the case: a typical grain has 12-14 sides; each side represents a boundary with a specific set of parameters (e.g. misorientation, inclination, energy and mobility). Accordingly, the boundary transition should be considered to occur at individual boundaries, not for complete grains.

Proposing the coexistence of boundaries with different mobility, different grain growth simulations showed that the slowest boundaries tend to dominate microstructural evolution [12, 32]. These studies argue that fast grain sides are slowed down by slow neighbors [12, 32, 33]. However, bimodal grain growth can still occur, if a critical number of grain sides exhibit the fast type [32]. Accordingly, the argumentation for bimodal microstructures in perovskite ceramics based on two boundary types still holds, but the relationship between the area fraction and the resulting microstructural appearance is more complex then discussed in this paper. Note that the average size of the population of small grains in Fig. 2 decreases slightly with increasing temperature. This possibly shows that even in the population of small grains still some fast grain boundaries exist (but do not cause bimodal

growth, since their fraction is below a critical number) and disappear gradually with increasing temperature.

Standard mean field approaches result in self-similar growth, i.e. the grain size distribution remains self-similar. This is obviously not the case in bimodal grain growth of perovskite ceramics. Accordingly a mean field approach using the mean grain size of a bimodal microstructure resulting in Arrhenius diagrams as shown in Fig. 1 allows for identifying grain growth transitions, but is not capable to quantify all details. For example a local variation of the driving force in bimodal microstructures is ignored in mean field approaches. Thorough grain growth simulations are needed to fully understand grain growth in perovskite ceramics.

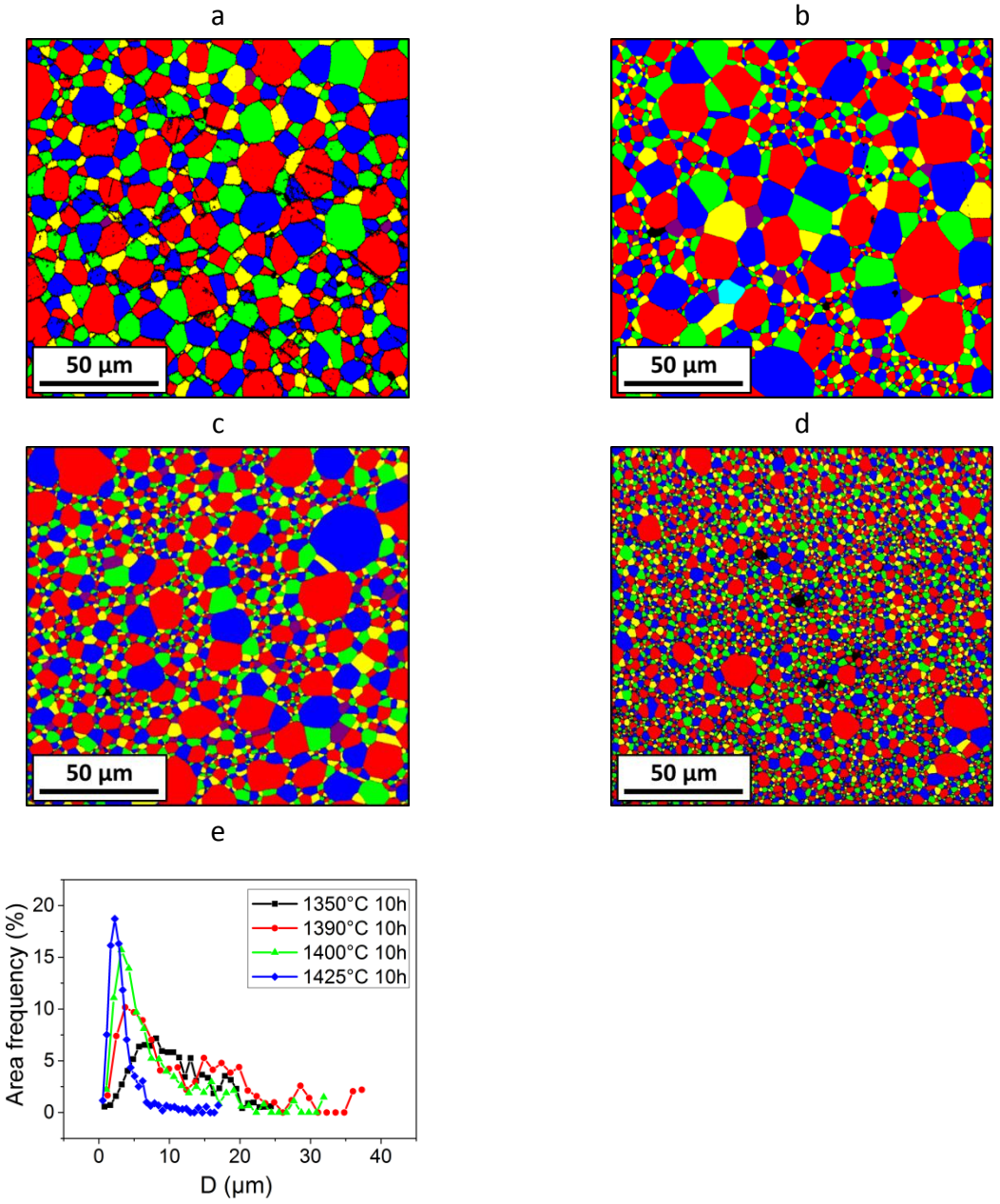

Figure 2: Microstructures of strontium titanate after 10h at 1350°C (a), 1390°C (b), 1400°C (c) and 1425°C (d) along with the respective grain size distributions (e) [11].

3. Impact of grain boundary anisotropy and grain growth transitions in perovskites

The interfaces of perovskite ceramics are not isotropic; both energy and mobility are anisotropic. This results in a texture of the grain boundary planes in polycrystals. In general five parameters are needed to classify boundaries [34]; accordingly anisotropy is a complex issue. However different assumptions can be made to decrease the complexity. Two will be discussed in the following.

3.1. Grain boundary energy anisotropy

The grain growth transitions of strontium titanate (Fig. 1a) and barium titanate (Fig. 1e) are related to a gradual transition of the grain boundaries from type 1 to type 2. This gradual transition of the boundaries is most likely caused by the anisotropy of the grain boundary energy [11]. A grain boundary will change its type, if the grain boundary energy is lowered. For example, in yttria, different grain boundary types were shown to have different grain boundary energies [25]. If the grain boundary energy is anisotropic, a variation of the individual transition temperature is plausible.

However, the grain boundary energy anisotropy is very hard to access directly, in particular due to the complexity of a five parameter space. The observation of dihedral angles of grain boundaries intersecting the surface (thermal grooving) can show differences in the grain boundary energy for different grain boundary types [25]. Most studies focus on the surface energy anisotropy and assume the grain boundary energy to be the sum of two surface energies less a binding energy [34]. For strontium titanate the surface energy was extracted from thermal grooves to obtain the Wulff shape [35].

Another possibility is the observation of the grain boundary plane distribution (GBPD): the frequency of a grain boundary plane with a given orientation is inversely correlated to its energy [34]. This method was used for strontium titanate at different temperatures [36, 37]. The most frequent orientations (i.e. lowest energy orientations) were found to be {100}, {110} and {111} (cf. Fig. 3), which is in good accordance with the Wulff shape observed by the shape of small pores (Fig. 4 [36]). While the GBPD data indicate an increasing anisotropy with increasing temperature (in Fig. 3 particularly the frequency of {100} increases with temperature), the inverse was found for the pore shape (Fig. 4). This could be caused either by a change of the absolute surface energy with respect to the binding energy [36] or a kinetic influence on the microstructures used to extract the GBPD. However, no strong change of the surface energy anisotropy in the temperature range of the grain growth transition was found; therefore the grain boundary mobility needs to be considered as well.

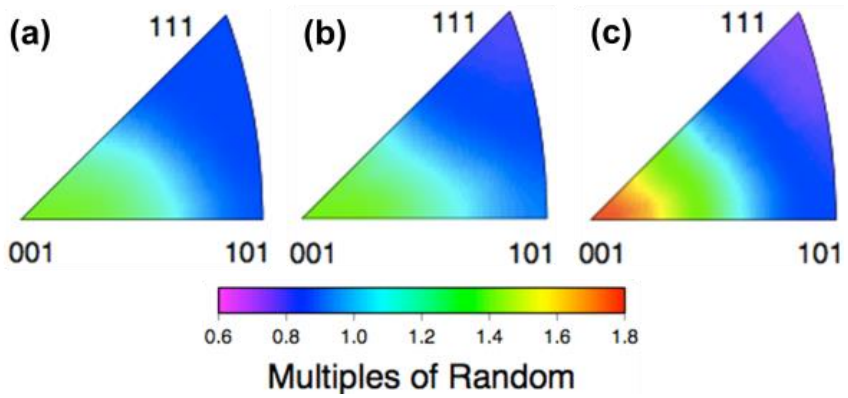

Figure 3: Grain boundary plane distribution of strontium titanate at 1300°C (a), 1350°C (b) and 1425°C (c) [36].

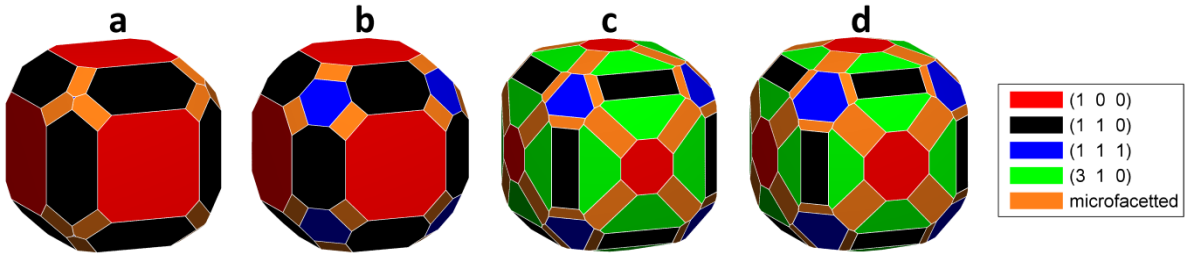

Figure 4: Wulff shape obtained by the shape of small intragranular pores at 1250°C (a), 1380°C (b), 1460°C (c) and 1600°C (d) [36].

3.2. Grain boundary mobility anisotropy

Special experimental setups are needed to obtain the anisotropy of the grain boundary mobility without an interaction with the grain boundary energy. Two recent studies revealed the growth of single crystalline seeds into a polycrystalline matrix in strontium titanate (Fig. 5a [24, 28]). In this geometry, the polycrystalline matrix provides a driving force for the single crystal to grow into the polycrystal. The properties of the matrix are averaged in a mean field sense (i.e. a mean grain boundary mobility m and energy γ are used). This assumption leads to a grain growth law for the growth of the single crystals yielding the relative mobility of the single crystal [28]. This experiment was performed for different orientations, various temperatures and atmospheres. The results are shown in Fig. 5b.

While most of the data is very close to 1 (i.e. the mobility of the respective orientations is close to the mean mobility of the polycrystals), at 1460°C a much higher mobility of the single crystals was found. At this temperature polycrystals show bimodal grain growth with coexisting grain boundary types 1 and 2 [10]. It was argued that at 1460°C single crystals show fast type 1 growth, while the polycrystals shows a mix of type 1 and 2 growth [28]. So far this behavior is not understood in detail, but it delivers a simple method to examine type 1 growth in detail e.g. via high resolution TEM, since the grain boundary type is well controllable.

However, the microstructures provide more information than the anisotropy of the mobility. The interface of the single crystal shows a different morphology depending on its relative

mobility: low mobility orientations have flat interfaces, while high mobility orientations tend to realign to low mobility orientations [24, 26, 28]. Fig. 6 shows microstructures for growing single crystals with different orientations. Flat interfaces can be found for {110} at 1460°C and for {100} at 1550°C according to their low mobility (Fig. 5b). Fast orientations (particularly {111} at 1460°C as well as {111} and {110} at 1550°C) show wavy interfaces which locally realign to low mobility orientations as indicated by the highlighted by white lines in Fig. 6. Similar results were found for barium titanate [27, 38].

The impact of the grain boundary mobility on the grain boundary plane orientation results in a useful implication: the local grain boundary orientation seems to be governed by the growing side of the boundary. This is simply implied by the occurrence of a macroscopic realignment of parts of the interface to low mobility orientations. The realignment obviously depends on the lattice orientation of the growing crystal. If this assumption holds, the complexity of parameters needed to classify interfaces in polycrystals decreases from five to two similar to the approach that the grain boundary energy is a sum of surface energies [34]. Additionally, the calculation of a kinetic crystal shape analogue to the equilibrium crystal shape becomes possible.

Note that this dominance of the growing crystal seems to be visible in polycrystals as well. As discussed in section 2.2 the grain boundary type is constant during growth of large grains. This is remarkable, since the growth of large grains requires the dissolution of adjacent grains; hence the grain boundary character (e.g. misorientation) of an individual boundary changes during growth. This phenomenon could be understood, if the growing crystal is assumed to dominate the properties of a boundary. However, the mobility of interfaces may vary with the orientation of the dissolving grain as well. While form the present results it seems to be clear that the growing side of the boundary can be dominant, but further research is needed to estimate the impact of the shrinking grain on the grain boundary mobility.

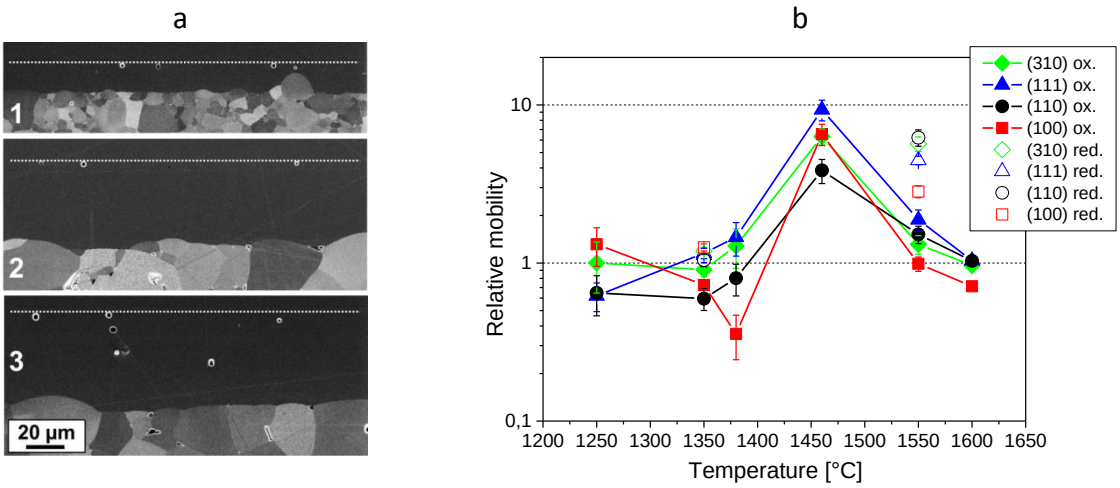

Figure 5: Growth of a single crystalline seed into a polycrystalline matrix at 1550°C after 6min (1), 1.5h (2) and 4.4h (3, a). The initial position of the interface is highlighted by white broken lines. Relative mobility obtained by the seeded polycrystals technique for different temperatures in oxidizing and reducing atmosphere (b) [24, 28].

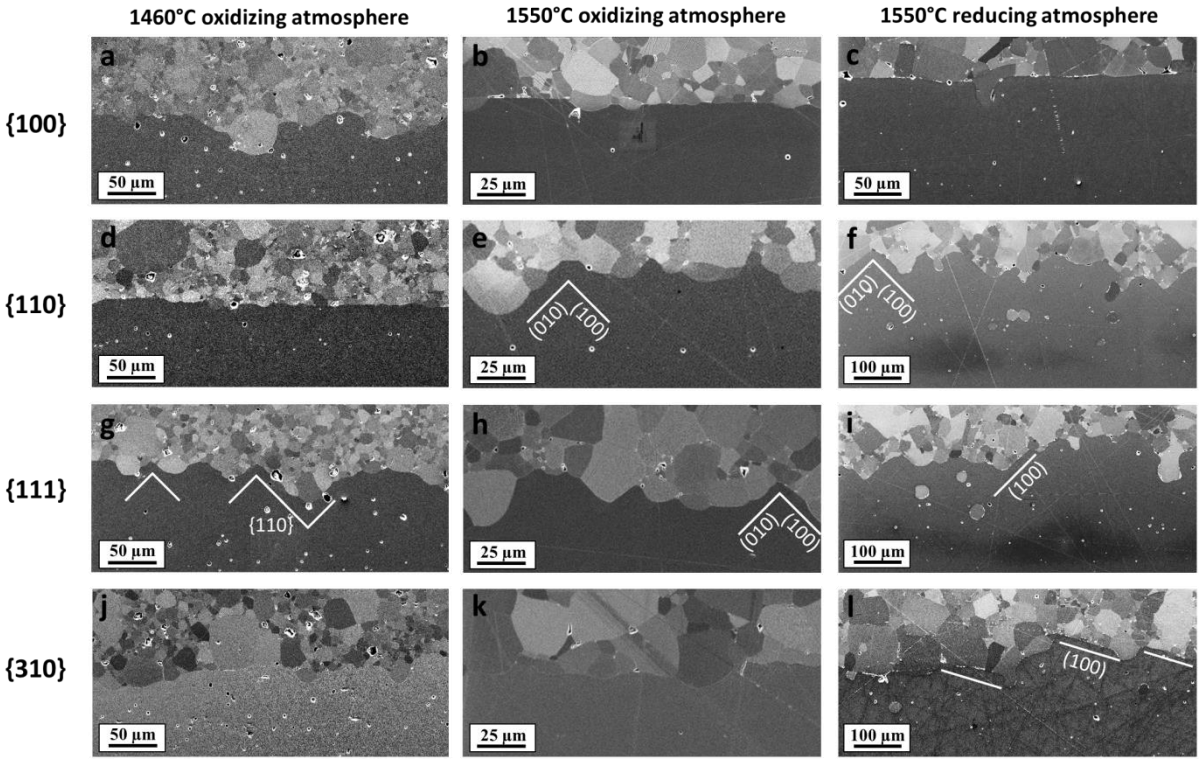

Figure 6: Interface morphology of single crystalline seeds at 1460°C after 40h in oxygen (a, d, g and j), at 1550°C after 0.4h in oxygen (b, e, h and k) and in 5% H_2 - 95% N_2 (c, f, i and l). The macroscopic orientation of the single crystal was {100} (a-c), {110} (d-f), {111} (g-i) and {310} (j-l). The white lines highlight a local realignment of the interface [24, 28].

3.3. The role of anisotropy in grain growth

The anisotropy of the grain boundary energy is important with respect to interfacial energy reduction, but a kinetic impact on the grain boundary plane exists as well. Consequently, from experiments it is not clear which anisotropy dominates the microstructural evolution of perovskites. Some grain growth simulations reveal that the boundary energy anisotropy dominates grain growth. These studies argue that the grain topology (i.e. dihedral angles and curvature) and, thus, driving force is not changed by the grain boundary mobility [32]. In contrast, a change of the grain boundary energy anisotropy would lead to a change in curvature and driving force; hence the grain boundary energy anisotropy is suggested to dominate microstructural evolution [32]. Other simulations show a much smaller effect of the energy anisotropy [39] or even a strong impact of the mobility [40].

Few experimental data allow balancing of the impact of energy and mobility anisotropy. Static experiments such as pore shapes or grain boundary grooving should represent equilibrium as defined by energetics. The grain boundary plane distribution (GBPD) is extracted from polycrystals which are generally in non-equilibrium. A kinetic impact on the data was addressed for strontium titanate and concluded to be small [41]. However the difference between the temperature dependent GBPD and the Wulff shape could be caused by kinetics: {100} was found to be more frequent at higher temperatures (Fig. 3). This orientation is also a low mobility orientation at high temperatures. Since grain growth is fast at higher temperatures, this could represent a kinetic impact on the boundary texture. It should be noted that if fast type 1 growth occurs, {100} is not a slow orientation (i.e. below

1350°C and at 1460°C, Fig. 5b). If slow type 2 growth occurs, {100} is the slowest orientation (i.e. at 1380°C and above 1550°C, Fig. 5b).
In summary, the exact correlation of anisotropy effects to grain growth transitions in perovskites remains unclear and it is not certain which anisotropy (energy or mobility) is dominant. Further experiments as well as simulations based on experimental datasets for interfacial anisotropy are needed to resolve possible energetic or topologic effects (i.e. a change of the boundary curvature with its type) for $SrTiO_3$.

4. Boundary structure in perovskites

4.1. Structure of boundaries in strontium titanate on the atomic scale

Extensive TEM studies analyzed the grain boundary structure of strontium titanate. However, most studies focused on special grain boundaries in bicrystals [42-44]. For general boundaries in high purity polycrystalline strontium titanate, the absence of grain boundary adsorption was documented as well [45-48]. At the atomic scale almost all boundaries are stepped; the step planes are commonly {100} and {110} planes [44, 45, 47-49]. Note that the same was observed on the macroscopic scale for example in the GBPD (cf. section 3.1).
Three studies focused on the difference of boundary structure between the two grain populations of bimodal microstructures [46-48]. A classification of boundaries into four different structural types was proposed (ordered flat, disordered flat, stepped and curved [47, 48]). However, no clear relationship between these four structures and the grain growth transition was observed. By trend, large grains (i.e. fast type 1 grain boundaries) showed more frequently ordered flat boundaries compared to small grains (i.e. slow type 2 boundaries). At temperatures below the grain growth transition, this trend does not seem to exist [46]. However, as discussed in section 3, this could also arise from kinetic reasons. Additionally, some evidence was reported for kinetic roughening on the atomic scale [50], but it is not clear if a correlation of fast type 1 boundaries with a specific boundary structure exists. Recent TEM work did not show a comparable trend [51].

4.2. Second phase segregation

Nanometer-thick disordered second phase films (“IGF”, intergranular glassy film) are known to exist in several types of ceramics, most prominently Si_3N_4 and alumina [52]. Their existence was also reported for strontium titanate [53-56]. These IGFs seem to be present only in materials with a low silica contamination [53, 56], but not for high purity strontium titanate as it is discussed here.
In barium titanate, a Ti-rich ($Ba_6Ti_{17}O_{40}$) second phase at some boundaries seems to cause exaggerated grain growth below the eutectic temperature of 1332°C [20, 57-62]. These exaggerated grains usually contain {111} twin lamellae, which seem to form preferentially if the second phase is present. The density of twinned exaggerated grains increases with increasing Ti-excess [58, 61]. The second phase has an epitaxial relationship to {111} planes of barium titanate [60]. Similar findings were published for barium strontium titanate [63]. Twinning in barium titanate coupled to second phase layers at the twin plane may probably cause a grain boundary energy reduction of {111} planes. It should be noted that the grain

growth transition of barium titanate coincides with the eutectic temperature of 1332°C (Fig. 1e).

Exaggerated grain growth dominated by {100} planes without the presence of twins was reported for stoichiometric barium titanate and equiaxed exaggerated grain growth seems to occur above the eutectic temperature [12, 20, 60, 61]. The impact of boundary structure on the grain growth transition (Fig. 1e) is still unclear and further investigation of bimodal grain growth is highly needed.

4.3. **Wetting transitions**

In some perovskites the grain growth transition can be correlated to a bulk wetting transition, as it was observed in strontium titanate [24] and LLTO [11]. Wetted boundaries occurred in strontium titanate during annealing in reducing atmosphere (5% H_2 + 95% N_2) at 1550°C (Fig. 7a). The wetting second phase was found to be Ti-rich [24] and to result in a drastic increase of the grain growth rate (Fig. 1c) and in the formation of exaggerated grains. The increasing fraction of large grains with increasing temperature in the grain growth transition is shown in Fig. 9. This phenomenon can be attributed to an anisotropic wetting [24], where some boundaries are wetted prior to others and then exhibit high grain boundary mobility. The reversibility of wetting was shown by repeated annealing below and above the wetting temperature (Fig. 7a-d).

Similar findings were published for LLTO: a wetting second phase occurred at the interfaces above 1425°C. Again this second phase was found to be Ti-rich [11]. However, while in strontium titanate a strong increase of the grain growth rate was observed (transition 2 in Fig. 1c), the opposite was found for LLTO (Fig. 1g).

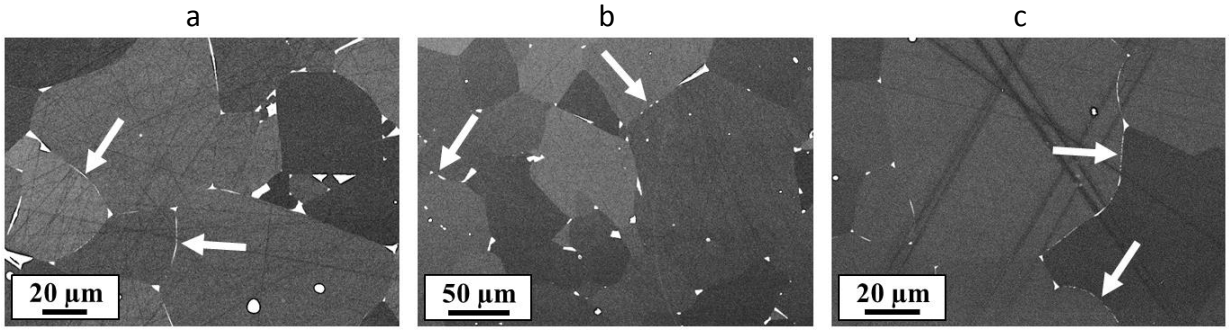

Figure 7: Microstructures of strontium titanate at 1550°C after 6min in 5% H_2 - 95% N_2 (a). The white arrows indicate a wetting second phase. The same sample was reannealed at 1350°C for 10h in 5% H_2 - 95% N_2 (b). The white arrows highlight second phase particles at the boundaries. The same sample was again reannealed at 1550°C for 2h in H_2 - 95% N_2 (c). The white arrows highlight a wetting second phase [24].

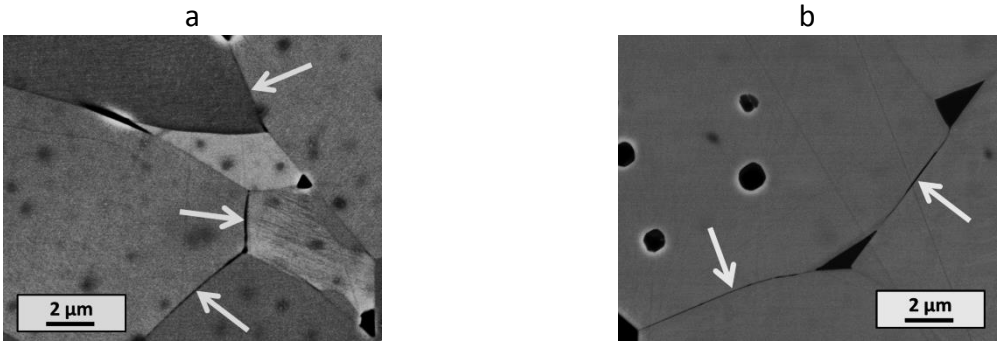

Figure 8: Microstructures of LLTO at 1425°C after 5h (a) and at 1450°C after 5h (b) in oxygen. White arrows highlight a wetting second phase [11].

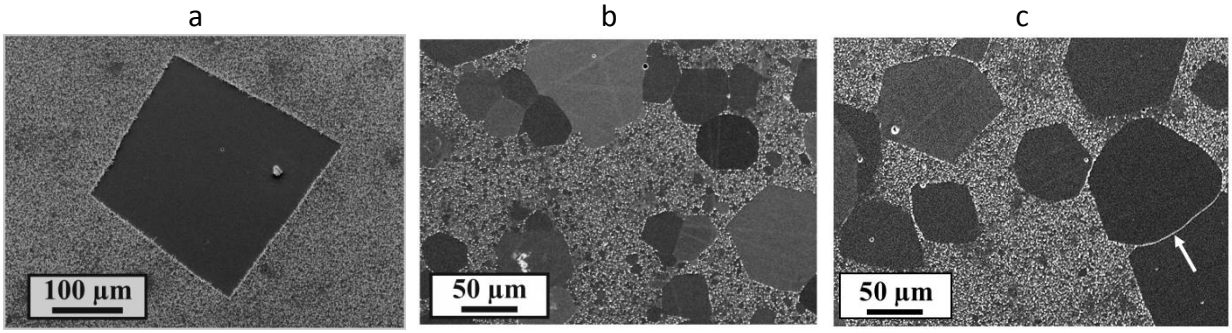

Figure 9: Bimodal microstructures in strontium titanate in 5% H_2 - 95% N_2 after 20h at 1460°C (a), after 1h at 1480°C (b) and after 0.5h at 1490°C (c) [24]. The arrow in c highlights a wetting second phase between two large grains. Note the increasing number of large grains.

4.4. Impact of faceting

In contrast to standard mean field modelling, a non-linear relationship between driving force and grain boundary velocity for grain growth was proposed for different perovskites [16, 17, 27, 61, 64, 65]. The idea is based on the energetic stability of boundaries facetted to low energy orientations. For boundary migration, a nucleus needs to form on the boundary planes. The energy needed for nucleation results in a nucleation barrier for grain growth [20, 21].

In this framework, facetted polycrystals can only grow, if the driving force overcomes the nucleation barrier. For driving forces in the order of the nucleation barrier, bimodal grain growth occurs, since the nucleation barrier can be overcome only locally by a limited fraction of grains. At higher driving forces unimodal grain growth occurs and low driving forces result in grain growth stagnation. Experimental evidence for this framework exists particularly for barium titanate [20, 27, 38, 62]. The grain growth behavior was explained by defect chemistry in a sense that a higher total vacancy concentration causes a decrease of the step free energy and a change in boundary morphology from facetted to rough [62, 66]. The total vacancy concentration was increased by donor doping, low oxygen partial pressures and an increasing temperature. For high defect concentrations normal grain growth and rough boundaries were found whereas for low defect concentrations facetted boundaries and bimodal grain growth or growth stagnation occurs. In pure barium titanate, bimodal grain growth was found only for temperatures below 1330°C [12]. Since vacancy concentrations increase with temperature as well, this is most likely caused by a thermal roughening

transition similar to the roughening transition with decreasing oxygen partial pressure or increasing donor dopant concentration. Thus, two boundary types could represent facetted ones (low temperature type) and rough ones (high temperature type). In this case, the gradual growth transition could be caused by a gradual grain boundary roughening e.g. related to the grain boundary energy anisotropy as discussed in section 3.1.
The effect could be similar in strontium titanate as well [26, 49, 67, 68], but faceting is different. Even in pure oxygen without any dopants, boundaries are not completely facetted; instead they reveal atomic steps [45]. Therefore, nucleation controlled growth does not seem to be important for bimodal grain growth in case of strontium titanate.

5. Grain boundary stoichiometry and space charge in strontium titanate

5.1. Grain boundary stoichiometry

In perovskite ceramics, grain boundary planes have a positive charge caused by excess Ti-ions [44, 69-72]. In the adjacent space charge, negative charge carriers are segregated (electrons, A-site vacancies and acceptors) and positive charge carriers are depleted (O-vacancies, holes and donors). B-site vacancies play no prominent role due to their high formation energy [73]. The result is a non-stoichiometry of the boundary, particularly of the A/B site ratio.
For strontium and barium titanate, several studies analyzed sintering or grain growth behavior with respect to the local or global A/B site stoichiometry. However, the mechanisms are very different for these materials. The phase diagram of barium titanate shows the existence of the line compound $Ba_6Ti_{17}O_{40}$. If excess Ti, thin segregation layers at boundaries form as discussed in section 4.2.
In strontium titanate a Sr-rich stacking fault (Ruddlesden-Popper-phase) exists, but seems not to interact with boundaries [45, 47]. No second phase segregation occurs in high purity strontium titanate (cf. section 4.1). Changes in grain boundary non-stoichiometry seem to be related to space charge effects. A relationship between the boundary stoichiometry and grain growth behavior was reported: above the grain growth transition, small grains preferentially have more Ti-excess at the boundaries than large grains [47, 48]. Thus slow type 2 growth seems to be correlated to a relatively low A/B ratio (and fast type 1 growth to a higher A/B ratio).
Although grain boundary chemistry is rather weakly connected to the overall material composition in perovskites, this microscopic effect agrees well with macroscopic material behavior. If the stoichiometry is varied extrinsically, bimodal grain growth as discussed in section 2 occurs for stoichiometric and Ti-rich compositions at temperatures above the grain growth transition. For Sr-rich compositions normal grain growth occurs, but at growth rates comparable to the population of large grains in stoichiometric and Ti-rich compositions [8, 47]. Thus the microstructural evolution with extrinsic variation of the stoichiometry agrees well with the TEM results and the assumption of the A/B ratio being different for the two boundary types of strontium titanate seems reasonable.

So far it is not known whether this A/B ratio is caused by a change of the space charge or a change of the boundary termination plane. Further experimental work is needed focusing on the boundary stoichiometry of the two different boundary types. As discussed in section 3.2, the fast type 1 growth of single crystalline seeds into a polycrystalline matrix provides a simple and reliable experiment for this task.

5.2. Grain growth stagnation: intrinsic drag on boundary motion

The theory of solute drag considers the effect of charged boundary cores and space charge layers on grain growth [74]. The space charge layer represents a segregation or depletion layer of charged defects (Fig. 10a). If gain growth occurs and boundaries move, two different scenarios appear. At low driving forces, the space charge layer migrates with the boundary (Fig. 10b and d). In this case, the diffusion of segregated defects limits the migration rate. If their diffusion coefficient is low, the migration can be drastically reduced. At very high driving forces, the boundary may break away from its space charge and move at high rates without such a drag effect (Fig. 10c).

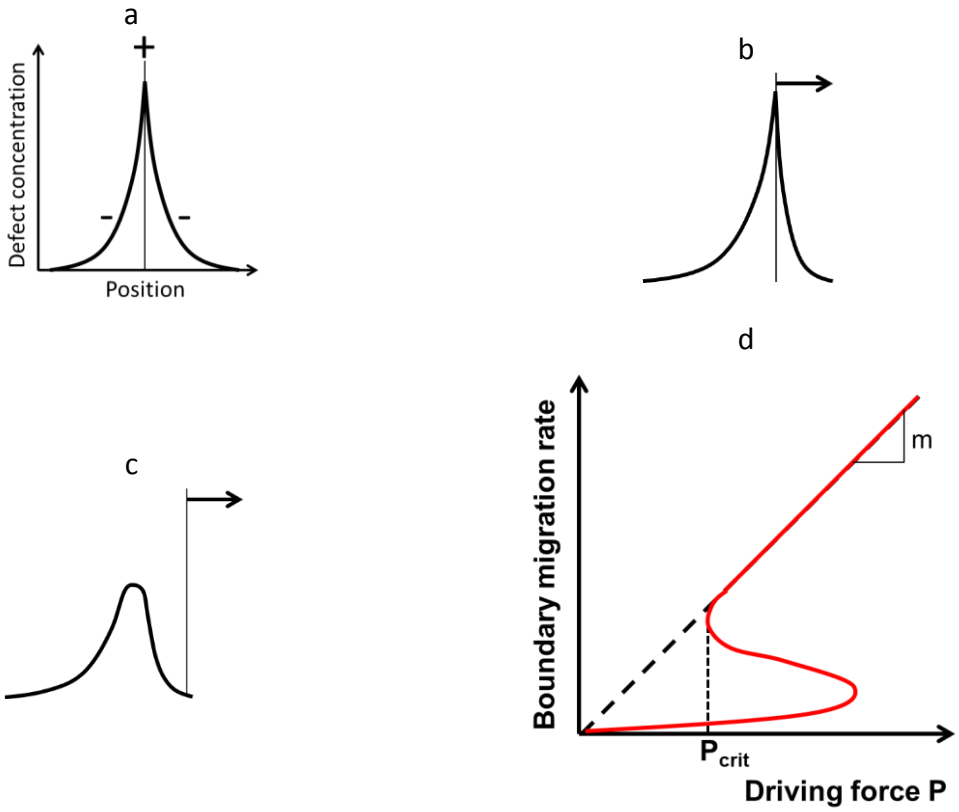

Fig. 10: Negative space charge at a positively charged boundary core (a). Distortion of the space charge profile by boundary migration at low driving forces results in solute drag (b). At high driving forces the boundary breaks away from the space charge (c). Relationship between the driving force and boundary migration rate in the framework of solute drag [74] (d). As in classical mean field modelling the grain boundary mobility m scales the boundary migration rate above the critical driving force P_{crit}.

Solute drag is known to occur in perovskites [75, 76]. However, an intrinsic drag similar to solute drag, but only based on intrinsic defects seems to exist as well. A segregation of Sr vacancies in the space charge was argued to cause a drag effect [24, 28]. The hypothesis is supported by experimental observations showing grain growth stagnation in high purity stoichiometric strontium titanate for all temperatures, but only in oxidizing atmospheres (Fig. 11).

In reducing atmosphere, the Sr vacancy concentration is very low, but the concentration of free electrons is high [73]. The opposite is true in oxidizing atmosphere. Therefore, in reducing atmosphere the negative space charge of strontium titanate is dominated by electrons and in oxidizing atmosphere by Sr vacancies. Since Sr vacancies move much slower than free electrons, an intrinsic drag effect similar to solute drag develops. Analogue to the solute drag effect, this intrinsic drag occurs at low driving forces (i.e. large grain sizes). During grain growth, the grain size increases and, thus, driving force for growth decreases. As soon as the driving force is below a critical value (P_{crit} in Fig. 10d), intrinsic drag effects occur and grain growth stagnates.

In general, a drag effect results in two different boundary states: a dragged state and a non-dragged state. It should be noted that these two states are not related to the two boundary types observed in strontium titanate. If they were related, slow type 2 boundaries should be in the dragged state. However, microstructures show that type 2 grains grow [10] and growth stagnation occurs independently of the growth type of the boundary at large grain sizes [28]. Nevertheless, an interplay of the intrinsic drag effect and the grain boundary type can be expected, since the boundary types seem to involve a change in the boundary A/B ratio.

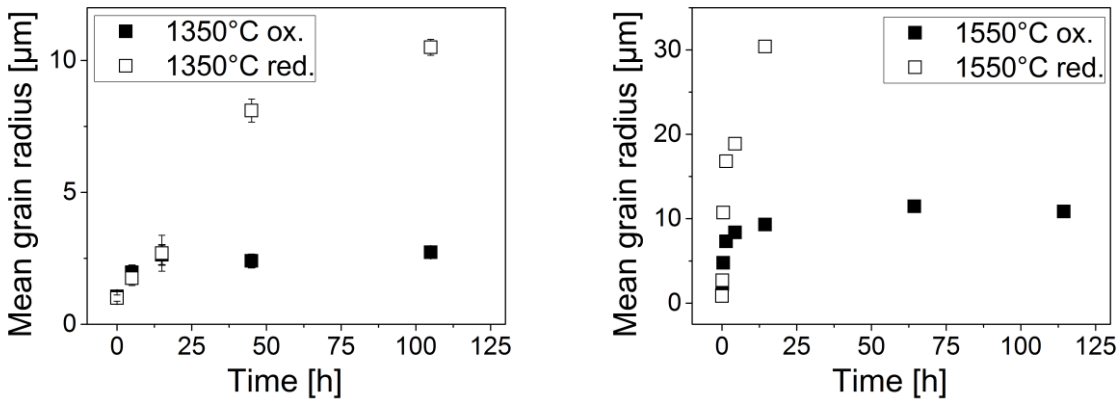

Fig. 11: Grain growth stagnation in polycrystalline strontium titanate at 1350°C (a) and at 1550°C (b). While in reducing atmosphere unlimited grain growth occurs, grain growth stagnates in oxidizing atmosphere (after 20h at 1350°C and after 5h at 1550°C).

6. Future directions and needed breakthroughs

Several issues are under debate. For strontium titanate, the difference between the two boundary types is still not well understood. Most probably a transition in the A/B ratio of the boundary occurs. This transition is probably coupled to boundary faceting and stepping as well. A simple access to this issue is the observation of boundary structure of single

crystalline seeds, since their growth is well-controllable in experiment (i.e. their growth type can be controlled by experimental parameters [28]). These experiments can provide well-defined samples for TEM investigation [45].

In alumina, dopants were shown to change the boundary properties drastically [1]. While some studies examine grain growth in perovskites with respect to dopant species [26, 62, 67, 76], no link to the boundary structure was established so far (cf. section 4). However, perovskites are more complicated than alumina due to more complex defect chemistry. Solubility limits can be very high and charge can be compensated by different mechanisms (A-site or oxygen vacancies, electrons, holes). Boundaries are charged and cause a depletion or segregation of defects. The boundary structure of perovskites needs to be analyzed not only by high resolution imaging, but also by high resolution chemical analysis. Particularly the impact of space charge and all related grain growth effects (solute and intrinsic drag) needs to be investigated in detail.

The growth transitions of perovskites highlight some general issues in grain growth as well. As in alumina, strontium titanate shows the same activation energy below and above the transition temperature. This leads to the question of what the thermal activated mechanism involves. Diffusion from a shrinking to a growing grain seems not to be fundamental. Possibly the activation energy is dominated by the interface reaction (e.g. activating to a different binding state at the boundary or breaking of bonds). In this case a change in the interfacial chemistry or a second phase film at the boundaries does not necessarily change the activation energy. The difference in growth rate of different boundary types could be related to a change of the boundary entropy [77]. However, more research on the mechanisms of boundary motion is needed.

To understand the growth behavior of different perovskites, thorough and valid grain growths simulations are needed. Particularly, the role of anisotropy needs to be investigated to clarify, which anisotropy (grain boundary energy or mobility) is dominant at which conditions. As discussed in section 3.2, the local grain boundary planes can be dominated by the growing side of the boundary. Accordingly, the set of parameters needed to understand or simulate growing polycrystals could be drastically reduced.

Finally, the existence of growth transitions in other perovskites should be analyzed. Best candidates are those systems showing bimodal grain growth, such as KNN [13-16] and NBT-BT [17, 18]. A comprehensive knowledge on the interface behavior of perovskites and its link to macroscopic factors is of high interest, since many applications need tailored microstructures and interfacial properties. A simple example is the ionic conductivity in LLTO, which highly depends on the boundary conductivity. Another example is a change in stoichiometry during processing due to evaporation of volatile species (e.g. Li and La in LLTO, Pb in PZT, Na and Bi in NBT-BT and K and Na in KNN). If the boundary type is linked to the boundary stoichiometry, careful control of the stoichiometry during processing is required to avoid bimodal microstructures.

7. Summary

Recent experiments show the existence of different grain growth transitions in perovskite ceramics. These transitions result in bimodal microstructures and seem to be caused by the existence and coexistence of different grain boundary types. Important factors for boundary and growth transitions are reviewed. The anisotropy was shown to be important, although it is not clear, whether (or at which conditions) the grain boundary energy or mobility is dominant. Different structural aspects of boundaries were discussed. In strontium titanate and LLTO (Lithium Lanthanum Titanate) a wetting transition appears. In barium titanate an epitaxial Ti-rich phase is important for bimodal grain growth and faceting or roughening plays a prominent role.

The understanding of growth transitions in perovskites needs to account for space effects. Charged boundaries of perovskites along with adjacent space charge seem to cause intrinsic drag effects on boundary motion. The boundary stoichiometry seems to be related to the boundary transition of strontium titanate. The two boundary types seem to differ in A/B site ratio.

Despite of thorough experimental investigation, some details of the grain growth transitions are still open e.g. for strontium titanate. Most of open questions relate to defects and their interaction with the boundary charge or structure. Since most cases among the broad field of applications of perovskite materials involve doping, a deeper understanding of the boundary transition behavior is needed for tailored microstructures and optimal materials properties.

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