Sintering and grain growth in SrTiO₃: impact of defects on kinetics

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The microstructural evolution of undoped and iron doped SrTiO₃ is analyzed during sintering at 1280°C in air and reducing atmosphere. The focus is on densification and grain growth during different holding times investigated by dilatometric studies and microstructural analysis. The sintering equations developed by Coble are used to characterize sintering. The influence of point defects on diffusion, densification and grain growth is evaluated using basic defect chemistry equations. A space charge concept at the grain boundaries is added to bulk defect chemistry concepts to understand sintering of perovskites, since the major part of mass transport during sintering occurs in this region. The extension of the defect chemistry concept allows to explain the change in diffusion mechanism during sintering (grain boundary diffusion or bulk diffusion) as well as grain growth stagnation observed in iron doped SrTiO₃. The results are used to separate the complex interplay of densification and grain growth. While grain growth decreases with increasing defect concentration, no clear trend is observed for the densification kinetics, since both grain growth and diffusion are relevant. The results show that grain growth during sintering provides comparable results to grain growth experiments in dense SrTiO₃ and, thus, pore drag seems not to be important. The calculated diffusion coefficients are in good agreement with literature data and show a strong dependency on the concentration of strontium vacancies.

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1. Introduction

Perovskite ceramics are widely used in different electronic applications as actuators (e.g. Lead zirconate titanate, Pb-[Zr_xTi_{1-x}]O₃), sensors (doped Strontium titanate, SrTiO₃), and high-permittivity dielectrics (Barium titanate, BaTiO₃).^{1,2)} During processing and sintering, the main characteristics of the materials such as microstructure and defect structure are defined. As these microscopic properties influence the macroscopic performance of the material, knowledge on the evolution of the microstructure during processing is of great importance. Changes in the electrical conductivity from insulating to conducting by addition of dopants and variations of the resistance of the material due to the influence of grain boundaries are examples showing that tailoring the sintering process and, hence, the microstructure is crucial to achieve the required material properties.

In the past decades, SrTiO₃ has established as a model material for perovskite ceramics. Accordingly, basic properties, such as defect chemistry,^{3–6)} ionic conductivity,^{1,3,7–11)} diffusion properties^{12–16)} and atomic structure of interfaces^{17–24)} are well-known. A set of reaction constants for high temperature bulk defect chemistry (1000–1400°C) was measured by Moos and Haerdtl.⁶⁾ By using TEM analysis, Chiang and Takagi^{17,18)} proposed a model for grain boundaries based on a positive Ti-rich grain boundary core and a negative space charge layer. Impedance data,²⁵⁾ SIMS (Secondary ion mass spectrometry) measurements¹⁰⁾ and simulations⁵⁾ provide detailed data of the space charge properties. The typical width of the space charge region ranges from several nanometers up to 100 nm and the

potential at the grain boundary is commonly determined as 0.4–1.0 V. A set of diffusion data for Ti and Sr in SrTiO₃ single crystals is presented by Goemann et al.^{15,16)} which indicates that both species diffuse via strontium vacancies at high temperature. Data for strontium vacancy mobilities are presented by Poignant and Juda²⁶⁾ for polycrystalline (Sr,Ca)(Ti,Nb)O₃ and Meyer et al.²⁷⁾ for single crystalline SrTiO₃.

In particular, several studies are published on the microstructural evolution (i.e. densification and grain growth) of SrTiO₃.^{28–35)} Densification was investigated regarding the influence of the Sr/Ti stoichiometry.^{28,32)} For materials with Sr-excess grain growth seems to dominate the microstructural evolution even during densification, while in Ti-rich materials densification is followed by grain growth. Both authors explained their findings with the influence of Sr-excess and the formation of Sr-vacancies leading to a decreasing diffusivity in the material. The appearance of a non-Arrhenius grain growth behavior^{29,33)} is another important fact for the development of the microstructure: Decreasing grain growth rates are found between 1350 and 1425°C leading to bimodal grain growth. While the phenomenon is not yet fully understood, the influence of the grain boundary energy,³⁴⁾ mobility³⁵⁾ and structure^{30,31,36,37)} are examined to find a proper explanation.

An analytical model to characterize the microstructural evolution during sintering was given e.g. by Coble^{38–40)} linking densification with grain size and diffusion coefficient. Changes in the microstructural evolution can be interpreted in two ways following the simplified coble equation

$$\dot{\rho} = C \cdot D / G^m \quad (1)$$

with a constant C , the mean grain diameter G and the diffusion coefficient D . The exponent m depends on the dominating

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diffusion mechanism and is $m = 3$ for volume diffusion and $m = 4$ for boundary diffusion.^{38),39)}

A variation in the densification behavior can be attributed to the diffusion coefficient D and diffusion mechanism or is caused by a change in the driving force by curvature, free surface area or interfacial energies. The diffusion coefficient may be changed by defect chemistry, while the free surface area depends on the interaction of grain growth and densification for the studied material. While these effects will be treated separately in the following, they are strongly linked to each other during microstructural evolution.

This present study uses the sintering model by Coble to analyze the intermediate stage of sintering in SrTiO₃. To separate the impact of densification and grain growth, iron doping was used to suppress grain growth. Comparing the sintering process at different dopant levels and in reducing atmosphere offers the possibility to evaluate the influence of defect chemistry on diffusion, densification and grain growth. For grain growth some investigations explained changes in microstructure by the total defect concentration.^{41),42)} While these studies focus on oxygen vacancies, we propose strontium vacancies as dominant defect species for diffusion, densification and grain growth as proposed by Goemann et al.^{15),16)} We also consider the existence of an internal space charge layer at the grain boundaries^{17),18),23),43)} to explain some of our findings.

2. Experimental procedure

Ceramic powders were prepared by the mixed oxide/carbonate route using SrCO₃ and TiO₂ as raw materials (purities of 99.95 and 99.995%, respectively; Sigma Aldrich Chemie GmbH, Taufkirchen, Germany). As acceptor dopant Fe₂O₃ (purity >99%, Merck, Darmstadt, Germany) was used. For the undoped material the molar ratio of Sr/Ti was 0.996; for the doped samples the Sr/Ti ratio was 1 with Fe dopant concentrations of 2 and 5 at-% with respect to the B site. Note that due to Zr abrasion during milling all powders have a slight Ti excess.²⁸⁾ The mixtures were milled with zirconia milling balls (2 mm) and 2-propanol in an attrition mill. Calcining was done at 975°C for 6 h in air. The results of the process were confirmed by XRD measurements, showing crystalline SrTiO₃ with no detectable second phase for all compositions. Particle diameters smaller than 1 μm (median diameter 0.5 μm) result from 16 h milling with zirconia milling balls (10 mm) and 2-propanol in a planetary mill. The particle size was measured by laser diffraction (Particle Size Analyzer 1064, Cilas, Orléans, France). SEM imaging provided information on morphology and agglomeration of powders.

Cylindrical green bodies for the dilatometer experiments were uniaxially pressed in a steel die and subsequently cold-isostatically pressed at 400 MPa. Green bodies showed densities between 61.2 and 63.8% as calculated from geometry. Samples were approximately 12 mm long and 8 mm in diameter.

Sintering experiments were conducted in a single rod dilatometer (402 E/2, Netzsch, Selb, Germany) in air and 80% Ar₂–20% H₂ forming gas (constant flow of 15 l/h) with a constant heating rate of 60 K/min to 1280°C followed by various dwell times (5–240 min). The low temperature was chosen to achieve slow sintering and to avoid the grain growth anomaly above 1300°C.^{29),33)} To compensate the thermal expansion of the alumina rod, a sapphire standard with 10 mm length was measured for each sintering setup. All sintering experiments were corrected with this data.

The density was determined by the Archimedes method after sintering. Every sintered sample was prepared for SEM imaging

to observe microstructural appearance. Samples were cut and polished with different diamond grinding discs (30–2 μm) and cloths (1 and 0.25 μm, polycrystalline diamond slurry). Polished samples were thermally etched at 1075°C for 2 h. The average grain size was measured at more than 500 grains per sample (AnalySis, Olympus, Japan).

3. Results and discussion

3.1 Powder characteristics

The particle size distributions and the corresponding SEM images of the powders are shown in Fig. 1. The median grain size (d_{50}) is between 0.4 and 0.6 μm and is smaller for the iron doped material. SEM images indicate small differences in the particle morphology: while undoped particles are more isotropic, iron doped particles show a slightly plate-like geometry. The primary particle size as estimated from SEM images is 0.2 μm and therefore smaller than obtained by laser diffraction, which is most likely caused by a slight agglomeration of particles.

3.2 Densification and microstructural evolution

In Fig. 2, densification is compared for the different materials and sintering atmospheres. For the same temperature profile, the 2% Fe-doped powder shows higher densification compared to the undoped material, while 5% Fe-dopant leads to a drastic decrease in final density. In reducing atmosphere, densification of undoped SrTiO₃ is lower than in oxidizing atmosphere. The isothermal densification rate reveals the significant difference in densification characteristics [Fig. 2(b)]. All compositions have comparable initial densification rates and show a decreasing rate with time. This decrease is caused by the reduction of free surface area during sintering and, thus, a decrease of the driving force. In reducing atmosphere, undoped SrTiO₃ shows slightly higher densification rates compared to sintering in air. With higher acceptor dopant concentration sintering rates decrease.

However, Fig. 2(a) only shows densification over time, but ignores a change of the driving force for sintering caused by grain growth and densification. Therefore, the densification rate for

Fig. 1. Particle size distribution for undoped and iron doped SrTiO₃ powder (a). SEM images of the undoped (b), 2% iron doped (c) and 5% iron doped powder (d).

Fig. 2. Temperature and relative density for 120 min isothermal cycles of undoped and doped materials in different sintering atmospheres (a). Densifications rates during the isothermal dwell time (b).

different dwell times during isothermal sintering is shown in Fig. 3 with respect to grain size (a) and density (b).

Figure 3(a) allows for discriminating the dominant diffusion mechanism by observing the slope of the fitted lines: Volume diffusion results in a slope of $m = 3$ and grain boundary diffusion in $m = 4$.³⁹⁾ Accordingly, for doped and undoped samples sintered in air, boundary diffusion seems to be dominant, while undoped material in reducing atmosphere shows a lower slope indicating a volume diffusion mechanism. At a grain size of 0.3 μm , the densification rate of undoped SrTiO₃ is highest, while iron doped materials show significantly lower densification rates, which is in good agreement with the trend in Fig. 2. Since densification rates are very different at the same mean grain size (i.e. at similar driving forces), the diffusion coefficients must be different as well; even the dominant diffusion mechanism changes [blue and black curves in Fig. 3(a)].

For a dopant concentration of 5% Fe, grain growth is inhibited completely; accordingly the sintering equations by Coble³⁹⁾ do not allow a determination of the dominant diffusion mechanism. The effect of growth stagnation is known for undoped material as well, but at much larger grain sizes³⁵⁾ and will be addressed later.

The decrease in free surface area and, therefore, the sintering rate cannot only be attributed to grain growth, but also to the increase in density (i.e. a change in free surface area). Accordingly, Fig. 3(b) shows the densification rate with respect to relative density. All curves (but not for 5% Fe dopant) are very similar indicating a similar dependence of the densification rate from the free surface area. The decrease of the densification rate in 5% Fe-doped SrTiO₃ is only related to the relative density, since no grain growth occurs. In contrast to Figs. 3(a) and 2(b), 2% Fe-doped material now shows the highest densification rates.

To capture microstructural appearance, Fig. 4 shows SEM

Fig. 3. Densification rate with respect to grain size (a) and relative density (b).

images of short and long dwell times. For the undoped material [Figs. 4(a)–4(d)], no significant change with atmosphere or dwell time can be observed other than an increase in density or grain size (cf. Figs. 2 and 9). With increasing dopant concentration, a drastic change in the microstructure evolution occurs: For 2% Fe-doped material [Figs. 4(e) and 4(f)], a much finer pore and grain size distribution is observed in the initial state of sintering. For long dwell times [Fig. 4(f)], still a small, but bimodal grain size distribution is found with very small pores located at triple junctions. For 5% Fe-doped samples, nearly no grain growth occurs; the mean grain size is the same in Figs. 4(g) and 4(h). However, the morphology in Figs. 4(g) and 4(h) is very different from Figs. 4(a)–4(f): Densification occurs in clusters, which are sintered to almost full density. In between, pores appear with a much larger size than the average grain size. Note that, ignoring the pore size, the mean grain size would imply fast shrinkage, which does not occur according to Fig. 2. This effect is most likely related to the morphology of pores and will be discussed in Section 3.4.

Figure 5 gives the relationship between grain growth and density. Although grain growth is slightly faster in reducing atmosphere, no strong impact of the atmosphere was found and grain growth occurs simultaneously with sintering. For 2% Fe-doped SrTiO₃, no significant grain growth is visible below 80–85% relative density. Subsequently, as shown in Figs. 4(e) and 4(f), single grains start to grow leading to an increase in the mean grain size accompanied by further densification. No grain growth occurs for the 5% Fe-doped SrTiO₃.

3.3 Diffusion and defect chemistry in sintering

In general, the Coble model allows for evaluating diffusion coefficients. The values are calculated with Eq. (1) for bulk

Fig. 4. Microstructures after short (10 min, top) and long (120 min, bottom) dwell times for undoped SrTiO₃ in air (a, b) and reducing atmosphere (c, d), 2%-Fe doped SrTiO₃ in air (e, f) and 5%-Fe doped SrTiO₃ in air (g, h).

Fig. 5. Evolution of the mean grain size during densification.

Fig. 6. Calculated diffusion coefficients based on Eq. (1) and densification rates (Fig. 3).

diffusion using the measured grain size and densification rates from Fig. 3(a). Following the suggestion by Coble,³⁸⁾ the constant C in Eq. (1) can be written as

$$C = \left[\frac{720\gamma\Omega}{k_B T} \right]. \quad (2)$$

The interfacial energy γ is assumed to be 1 J/m² and the atomic volume Ω is the volume of a perovskite unit cell (a_0^3)_{SrTiO₃} = 5.94 · 10⁻²⁹ m³. Since it is not possible to estimate a reasonable grain boundary width relevant for sintering, this parameter is a scale factor in the Coble equation for boundary diffusion; all calculations assume bulk diffusion to dominate during sintering.

The diffusion coefficients obtained from Fig. 3(a) are shown in Fig. 6. For the undoped material the diffusion coefficient is independent of grain size, while with increasing dopant concen-

tration lower diffusion coefficients are obtained with increasing grain size.

In the literature, the lattice diffusion coefficient of Sr in SrTiO₃ was measured by tracer methods and was found to be in the order of 10⁻²³–10⁻²⁰ m²/s at 1280°C.^{15),16)} In the present sintering experiments the diffusion coefficients are higher by two orders of magnitude at the same temperature. However, higher diffusion coefficients in sintering experiments compared to tracer data are well-known;^{40),44),45)} this is probably attributed to the influence of the microstructure and the difference in the driving force between the experimental setups. The Coble equation bases on many assumptions and should only be seen as an order of magnitude approach to characterize diffusion.³⁹⁾

Nevertheless, an additional explanation for this behavior can be extracted from the defect chemistry of SrTiO₃. For a diffusion of Sr via A-site-vacancies ($[V_{Sr}'']$) the general relationship between the diffusion coefficients for Sr D^{Sr} and Sr-vacancies $D^{V_{Sr}''}$ is

$$D^{Sr} = \frac{[V_{Sr}'']}{[Sr_{Sr}^x]} \cdot D^{V_{Sr}''} \quad (3)$$

While Ti is the slowest species, its diffusion is coupled to the strontium vacancies,^{15),16)} hence Eq. (3) can be used as an estimation for the diffusion coefficient relevant for sintering.

Taking into account the simplified defect chemistry for bulk SrTiO₃, the following cases have to be distinguished.

- i. The thermally activated vacancy concentration for undoped SrTiO₃ in air is:

$$[V_{Sr}''] \approx C_V \cdot e^{\left(-\frac{E_V}{k_B T}\right)} \quad \text{for a constant } p_{O_2} \quad (4)$$

Equation (4) indicates increasing strontium vacancy concentration ($[V_{Sr}'']$) with increasing temperature T . C_V is a constant and E_V is the activation energy for strontium vacancy formation.

- ii. In reducing atmosphere $[V_{Sr}'']$ decreases for undoped SrTiO₃ with decreasing oxygen partial pressure:

$$[V_{Sr}'']^{\frac{1}{2}} \approx p_{O_2} \quad \text{for a constant } T \quad (5)$$

According to Eq. (5) and the high temperature (1450°C) defect chemistry of SrTiO₃,⁶⁾ a decreasing oxygen partial pressure (p_{O_2}) from 1 to 1 · 10⁻¹⁵ bar (which corresponds to our reducing atmosphere of 80% Ar₂–20% H₂) results in a decrease of the strontium vacancy concentration

Fig. 7. Scheme of the possible impact of space charge zones on the diffusion at different sintering conditions and grain sizes.

($[V_{\text{Sr}}'']$). Following Eq. (3) this leads to a reduction of the diffusion coefficient by about two orders of magnitude.

- iii. For acceptor doped SrTiO₃ [V_{Sr}''] decreases with increasing dopant concentration:

$$[V_{\text{Sr}}''] \sim \frac{1}{[A']} \quad \text{for a constant } T \text{ and } p_{\text{O}_2} \quad (6)$$

Following Eq. (6) the strontium vacancy concentration ($[V_{\text{Sr}}'']$) is inversely proportional to the acceptor dopant concentration ($[A']$). This accords well to the decrease in the mean diffusion coefficients from $8 \cdot 10^{-18} \text{ m}^2/\text{s}$ for the undoped SrTiO₃ to $8 \cdot 10^{-21} \text{ m}^2/\text{s}$ for the 5% Fe-doped material as obtained by the Coble equation (Fig. 6).

The space charge theory provides a possible explanation for the change of the diffusion mechanism shown in Fig. 3(a). SrTiO₃ is well-known for a positive charge of the Ti-rich grain boundary core^{(7),(17),(18)} resulting in a negative space charge. Following a model proposed by Yan et al.⁽⁴³⁾ on KCl, this may lead to an enhanced diffusion in the space region (Fig. 7). In undoped SrTiO₃ the space charge region has an extent of 20–30 nm at high temperatures.⁽¹⁷⁾ According to space charge theory a collapse of the space charge layer thickness occurs with higher defect concentrations due to an increasing temperature, with decreasing oxygen partial pressure [Fig. 7(b)] or doping [Fig. 7(c)]. Therefore, the width of the region of enhanced diffusion at the boundaries decreases with increasing defect concentration. At equal grain sizes this decrease could even lead to a transition from grain boundary diffusion to volume diffusion with increasing defect concentration [Fig. 7(b)], as it is observed when the sintering atmosphere is changed from oxidizing to reducing conditions [Fig. 3(a)]. This change of the diffusion mechanism may superpose the bulk defect chemistry as described above.

For 2% Fe-doped SrTiO₃ the grain size is very small due to grain growth stagnation. Since the space charge layer width is independent of grain size, their width with respect to grain size seems still to be large enough to sustain grain boundary diffusion as dominant mechanism for densification [Fig. 7(c)]. For a 5% Fe-doped material the Coble model is not applicable to obtain information on the diffusion path, since no grain growth occurs.

3.4 Impact of microstructural evolution on densification

The SEM micrographs in Fig. 4 and the densification curves in Fig. 2 indicate the importance of microstructural changes: For 5% Fe-doped SrTiO₃, fast shrinkage would be expected due to the very small grain size (Fig. 5). However, densification ends below 80% relative density. Microstructures show only for the 5% doped samples a pore size much larger than the grain size [Figs. 4(g) and 4(h)] as well as densified regions between these

large pores. Also the 2% Fe-doped sample indicates a different densification behavior (Fig. 2) and microstructural evolution compared to the undoped material. This paragraph argues that the grain growth stagnation in 5% Fe-doped SrTiO₃ is the key to understand this behavior.

The driving force for densification and grain growth is given by the free surface or grain boundary energy and the curvature of the material. We assume the surface energy as constant and independent of the defect chemistry (i.e. dopant and atmosphere). This seems to be reasonable as the variations of the surface energy reported for SrTiO₃ and Al₂O₃^{(44),(45)} are small with respect to their impact on the Coble equation. The free surface area in powder compacts can be reduced by densification and grain growth. Grain growth decreases the driving force available for sintering, since the curvature decreases. Thus sintering and grain growth are conflictive processes. As discussed below, the changes in microstructural evolution (Fig. 4) can be explained by a different interaction between grain growth and densification.

In the undoped material the microstructural evolution is almost independent of the atmosphere. The densification rates show similar behavior with increasing grain size and increasing density. Both grain growth and densification occur simultaneously (Fig. 5), but grain growth is slightly emphasized in reducing atmosphere. The lower densification in reducing atmosphere can be explained by change of the diffusion mechanism [different slope in Fig. 3(a)] and a decrease in driving force due to faster grain growth. The opposite is found when small amounts of dopants are added: densification increases while grain growth is reduced. Normally, a higher driving force for densification is expected when grain growth slows down, but the experimental data in Figs. 2(b) and 3(a) indicate much lower densification rates for the Fe-doped samples. Note that the densification rates decrease with increasing Fe-concentration for equal grain sizes [Fig. 3(a)], but compared to undoped material the final densities are higher for SrTiO₃ with 2% Fe and much lower for SrTiO₃ with 5% Fe (Fig. 2). Lower densification rates with increasing dopant level support a decrease in the diffusion coefficient as proposed in section 3.3.

The microstructural evolution offers a possible explanation for this counterintuitive behavior. Pore shrinkage or pore growth depending on size and coordination number of pores is a well-known phenomenon.^{(46)–(48)} For a constant dihedral angle of 120° at triple junctions (i.e. six surrounding grains in two dimensions) the pore is stabilized [Fig. 8(b)]. Coordination numbers differing from six lead to unstable configurations with pore shrinkage for numbers smaller than six [Fig. 8(a)] and pore growth for numbers higher than six [Fig. 8(c)].

In undoped SrTiO₃ the coordination number of pores is almost always smaller than or equal to six [Fig. 9(a)], while for Fe-

Fig. 8. Sketch of the 2-dimensional pore stability for constant dihedral angles of 120° . A pore with less than six neighboring grains is unstable and shrinks (a), six neighbors result in a stable pore (b) and more than six neighbors in an unstable, but growing pore (c).

Fig. 9. Microstructure after 30 min at 1280°C of undoped (a) and 5%-Fe doped SrTiO_3 (b). For exemplary pores (black) attached grains are highlighted in red. Coordination numbers are added to the pores.

doped SrTiO_3 much higher coordination numbers occurs [Fig. 9(b)]. For the 2% Fe-doped material the concept of grain growth induced densification^{49),50)} seem to explain the obtained higher final densities. Due to bimodal grain growth above 80–85% relative density [Fig. 4(f)], larger pores can change their coordination number and are, therefore, reactivated to contribute to overall densification.

For the highly Fe-doped material densification occurs cluster-wise, resulting in large pores in relation to the grain size [Fig. 4(g)]. The shrinkage at small pores is very fast during the heating due to local curvature and driving force [Fig. 8(a)], while slightly larger, higher coordinated pores tend to grow [Fig. 8(c)]. Since further densification can only occur at small pores with lower coordination numbers, the overall densification rates are drastically reduced. This can be seen from Fig. 3(b): densification rates decrease by two orders of magnitude, whereas the overall densification is only 5%.

This inhomogeneous sintering is most likely caused by the pore size distribution of green bodies in a sense that the largest pores act as nuclei for pore growth. The result is a microstructure consisting of clusters with locally full dense regions and large pores surrounded by more than 10 grains [Fig. 9(b)] resulting in an overall density of less than 80%. The results clearly show that grain growth is not always contrary to densification due to a decrease of the driving force, but is at least needed to some extent to achieve high final densities.

3.5 Grain growth and sintering: impact of pore drag and solute drag

Not only has the densification to be considered to evaluate the microstructural evolution also grain growth plays an important role. **Figure 10** shows slightly higher grain growth in reducing atmosphere and a drastic decrease with increasing dopant level compared to undoped SrTiO_3 sintered in air. To quantify this effect, a standard grain growth law of the form

Fig. 10. Measured grain size after isothermal sintering with different dwell times. The data points are fitted with a cubic grain growth law [Eq. (7)].

Fig. 11. Grain growth coefficients obtained in this study compared to literature data of grain growth in dense SrTiO_3 .

$$G^2 - G_0^2 = k \cdot t \quad (7)$$

was used with the mean grain diameter G , the mean diameter G_0 at time $t = 0$ and the grain growth constant k .⁵¹⁾ The grain growth constant k is shown in an Arrhenius graph in **Fig. 11** as obtained by Fig. 10 and Eq. (7). Literature data on grain growth in dense undoped SrTiO_3 in air or oxygen is added. The grain growth constants are in good agreement with each other. Accordingly, grain growth during sintering is very similar to dense SrTiO_3 ; no significant pore drag effect is evident. Note that in Fig. 9 grain growth seems to follow parabolic kinetics. In general, drag effects are known to increase the exponent of the growth law to numbers greater than 2.^{52),53)}

For samples sintered in reducing atmosphere, grain growth is slightly faster than in air, which again fits literature data well.⁵⁴⁾ As in oxidizing atmosphere, pore drag seems not to be important.

As shown in Fig. 4, grain growth was strongly bimodal for 2% Fe-doped materials and stagnated completely for 5% Fe-doped samples. As discussed below, this can be explained by the theory of solute drag.^{55),56)}

The effect of solute drag bases on charged boundary cores with an adjacent space charge. In this space charge layer, different defects are depleted or segregated depending on their charge. If a dopant species is added to the system, it may segregate as well. If grain growth occurs and this boundary is moved, two different scenarios appear. At low driving forces, the space charge layer migrates with the boundary. In this case, the diffusion of segregated dopants limits the migration rate; if its diffusion coefficient is low the migration can be drastically reduced. However, at very high driving forces, the boundary may break away from its space charge and move at high rates without a drag effect.

For SrTiO₃, segregation of acceptor dopants towards the boundaries occurs^{[17),18),57)}, thus the occurrence of solute drag by iron dopants is likely in the present experiments. At 2% Fe-dopant concentration, a fraction of boundaries seems to have sufficiently high driving forces to break away from the solute drag. Those boundaries result in large grains and a bimodal grain growth occurs. At 5% Fe-dopant concentration, all boundaries seem to be dragged and no significant grain growth can be observed. However, a TEM examination of local iron concentration and its correlation to bimodal microstructures is needed to confirm the existence of solute drag in Fe-doped SrTiO₃.

4. Summary and conclusions

The present paper examines the impact of defect chemistry and grain growth on sintering kinetics and diffusion in SrTiO₃. The defect chemistry was modulated by the sintering atmosphere (i.e. oxygen partial pressure) and acceptor dopant concentration (i.e. iron). In general, both reducing atmosphere and acceptor doping result in a decrease of the strontium vacancy concentration. In previous studies the strontium vacancy concentration was shown to be rate-limiting for sintering, since all cations migrate via the A-site of the perovskite lattice.

The sintering process of undoped and Fe-doped SrTiO₃ was analyzed using the Coble model, which allows for discriminating the dominant diffusion mechanism. For undoped SrTiO₃, a change of the atmosphere leads to a transition from grain boundary diffusion in oxidizing atmosphere to volume diffusion in reducing atmosphere.

Diffusion coefficients extracted from sintering show a strong decrease with increasing dopant level, which corresponds well to a low strontium vacancy concentration as predicted by defect chemistry. This is most likely caused by the influence of a space charge with a positive boundary core and a space charge enriched in negative defects. According to this model, the strontium vacancies migrate towards the boundary and result in a much higher local concentration than predicted by bulk defect chemistry. Since mass transport during sintering occurs close to the boundaries, the space charge region at the boundaries is argued to enhance the sintering rate.

Increasing iron dopant suppresses grain growth and results in drastic changes of the microstructural evolution. A 2% Fe-doped SrTiO₃ reveals a microstructure with small, but bimodal grain sizes and high densification, whereas a 5% Fe-doped material indicates no grain growth and overall densification is drastically reduced. For this effect the pore coordination is found to be important. Under normal conditions the coordination number decreases during sintering and pores continuously shrink during grain growth. However, with suppressed grain growth, grains are much smaller than pores leading to high coordination numbers and pore growth. Between growing pores, full densification is obtained as revealed by the microstructures. However, to approve the impact of the microstructural evolution on sintering, careful

sintering simulations are needed considering the impact of the initial pore size distribution and grain growth on densification.

Grain growth stagnation resulting from Fe-doping is most probably caused by solute drag. Not only strontium vacancies, but also acceptor dopants are known to segregate to positively charged boundaries. Depending on the driving force, this segregation profile migrates with a moving boundary. Since iron diffusion in bulk SrTiO₃ is slow, a drag force on boundary migration occurs. At high Fe-concentrations (5%), this drag force seems to result in complete grain growth stagnation, while at lower Fe-concentrations (2%) some boundaries can still overcome the drag force and bimodal grain growth occurs. However, the existence of solute drag in Fe-doped SrTiO₃ needs to be confirmed by observing segregation profiles at different boundary migration rates by TEM. Pore drag seems not to be important in SrTiO₃, since grain growth during sintering (i.e. in very porous microstructures) is similar to dense polycrystalline material.

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