

# Cation self-diffusion of $^{44}\text{Ca}$ , $^{88}\text{Y}$ , and $^{96}\text{Zr}$ in single-crystalline calcia- and yttria-doped zirconia

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Self-diffusion of calcium, yttrium, and zirconium in single-crystalline YSZ and CSZ (YSZ: yttria-stabilized zirconia; containing 10 to 32 mol%  $\text{Y}_2\text{O}_3$ ; CSZ: calcia-stabilized zirconia; containing 11 and 17 mol% CaO) was measured at temperatures between 960 and 1700 °C. For zirconium and calcium diffusion, the stable isotopes  $^{44}\text{Ca}$  and  $^{96}\text{Zr}$  were used as tracers and the samples were analyzed with secondary ion mass spectrometry. In the case of yttrium diffusion, the radioactive tracer  $^{88}\text{Y}$  was used and an abrasive sectioning technique was applied. Zirconium bulk diffusion is slower than yttrium and calcium bulk diffusion, and there is a nearly linear correlation of diffusion coefficient with cation radius. In YSZ, zirconium and yttrium bulk diffusivity are maximum for a stabilizer content of 10–11 mol%, while in CSZ both calcium and zirconium tracer diffusion are independent of the calcium content. The activation enthalpy of yttrium stabilizer bulk diffusion (4.2 eV) is, as in CSZ, slightly smaller than for zirconium bulk diffusion (4.5 eV). The yttrium dislocation pipe diffusivity is five to six orders of magnitude faster than the bulk diffusivity, and its activation enthalpy (3.5 eV) is also smaller than that of the bulk diffusion. From the activation enthalpy and from the concentration dependence of the cation bulk diffusion, it is concluded that the cation diffusion occurs either via free vacancies ( $V_{\text{Zr}}^{4+}$  in YSZ) or via bound vacancies ( $[V_{\text{Zr}}^{4+} - 2V_{\text{O}}^{2+}]^x$  in CSZ). © 2003 American Institute of Physics. [DOI: 10.1063/1.1628379]

## I. INTRODUCTION

Stabilized zirconia exhibits very high oxygen ion conductivity and is therefore used as electrolyte material in high temperature applications. While there is a considerable amount of data available on the oxygen transport (see, e.g., Refs. 1 and 2), only little is known about the host and stabilizer cation transport in stabilized zirconia.<sup>3,4</sup> The very slow cation diffusion plays a crucial role in the understanding of key processes such as aging effects observed in the oxygen conductivity,<sup>1,2</sup> and of high-temperature mechanical behavior (internal friction,<sup>5</sup> creep<sup>6</sup>). Particularly, nothing is known about the self-diffusion of yttrium in yttrium-stabilized zirconia (YSZ). Only two sets of data have been obtained until now, which resulted essentially from interdiffusion experiments monitoring effectively the chemical diffusion: Sakka *et al.*<sup>7</sup> published measurements on chemical diffusion in YSZ containing different yttria contents, and Solmon *et al.* investigated the cation transport from the bulk into a thin Zr-rich

layer using secondary ion mass spectrometry (SIMS).<sup>3</sup> Both groups deduced indirectly that the yttrium transport must be faster than the transport of zirconium.

Cation diffusion in stabilized zirconias has recently attracted some interest by studying the diffusion of impurity cations into the material. In our own work, we investigated the diffusion of lanthanides, and found that the bulk diffusion coefficient ( $D_{\text{bulk}}$ ) is higher than that of zirconium, and increases with ionic radius of the lanthanides.<sup>8</sup> Activation enthalpies are in the range from 4.5 to 5.5 eV. Matsuda, Bak, and co-workers investigated the diffusion of  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  in YSZ and gave values for bulk, dislocation, and grain boundary diffusion coefficients.<sup>9,10</sup> Their values of bulk and grain boundary diffusion coefficients in YSZ are very high in comparison to the other available literature data, and they found very low activation enthalpies for the grain boundary diffusion [1.25 and 1.9 eV for  $D_{\text{GB}}(\text{Mg})$  and  $D_{\text{GB}}(\text{Ca})$ , respectively]. Kowalski *et al.* also looked at the diffusion of  $\text{Ca}^{2+}$  and  $\text{Ti}^{4+}$  in YSZ and measured both bulk and grain boundary diffusion coefficients.<sup>11</sup> They found distinct differences for the grain boundary diffusion of small cations and big cations: The activation enthalpy for  $\text{Ti}^{4+}$  bulk diffusion

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is much higher than for grain boundary diffusion (5.2 versus 3.5 eV), while this is reversed for  $\text{Ca}^{2+}$  diffusion (3.45 versus 3.8 eV). Waller *et al.* looked at the diffusion of  $\text{Mn}^{3+}$  in YSZ and found a much higher activation enthalpy for the grain boundary diffusion than for bulk diffusion.<sup>12</sup>

The cation diffusion in calcia-stabilized zirconia (CSZ) is even less experimentally investigated.<sup>13–16</sup> The available data suggest slightly larger diffusion coefficients but similar activation enthalpies in comparison to YSZ. Möbius *et al.*<sup>13</sup> reported to have observed very high bulk diffusion coefficients, but it is more likely that they measured the grain boundary diffusion and misinterpreted it as bulk diffusion. Rhodes and Carter<sup>14</sup> evaluated the bulk and the grain boundary diffusion in CSZ and observed that for both cations the grain boundary diffusion coefficients ( $D_{\text{GB}}$ ) are higher by a factor of  $10^4$  to  $10^5$  (between 1800 and 2150 °C) as compared to the corresponding bulk diffusion coefficients ( $D_{\text{bulk}}$ ). They estimated activation enthalpies for the bulk diffusion (Ca: 4.3 eV; Zr: 4.0 eV), but not for the grain boundary diffusion. In a recent attempt, we measured the diffusion of lanthanides in single-crystalline CSZ<sup>15</sup> and found a behavior qualitatively similar to lanthanide tracer diffusion in YSZ; that is, the diffusion coefficients were increasing with increasing ionic radius of the diffusing element, but the activation enthalpies were higher than in YSZ (5 to 6 eV), probably due to cation vacancy association.

In an earlier study we measured the bulk diffusion in CSZ, but were not able to investigate the grain boundary diffusion in that material due to experimental limitations.<sup>16</sup> Usually, stable isotope diffusion experiments are performed and the diffusion profiles are analyzed with SIMS. This method is fast and has a better spatial resolution than radiotracer experiments, but in the case of self-diffusion experiments, it is limited by the natural abundance of the rare stable tracers used. Since the commonly used isotopes of Ca and Zr have a relatively high natural abundance ( $^{44}\text{Ca}$ : 2.08%;  $^{90}\text{Zr}$ : 2.78%), it is difficult to detect the dislocation or grain boundary self-diffusion of these elements in stabilized zirconia using SIMS. On the other hand, the radiotracer method has the unique advantage that the natural abundance of radiotracers is principally zero, allowing for investigations of the dislocation or grain boundary self-diffusion. Its drawback is that the depth resolution is usually worse than for SIMS, allowing only measurements at higher temperatures.

In this article, we present yttrium tracer diffusion experiments (in the temperature range from 1400 to 1676 °C) yielding both bulk and dislocation diffusion coefficients in YSZ. These results are compared with Zr self-diffusion data for YSZ and with Zr and Ca self-diffusion data for CSZ.

## II. EXPERIMENTAL DETAILS

### A. Sample preparation and stable tracer experiments

YSZ single crystals (obtained from Zirmat Corp., Westford, MA, and Swarovski AG, Austria) containing 10 to 32 mol %  $\text{Y}_2\text{O}_3$  were cut into slabs of  $5 \times 5 \times 1 \text{ mm}^3$  and polished. The stable isotope  $^{90}\text{Zr}$  (2.78% natural abundance) was implanted with an energy of 150 keV and a dose of

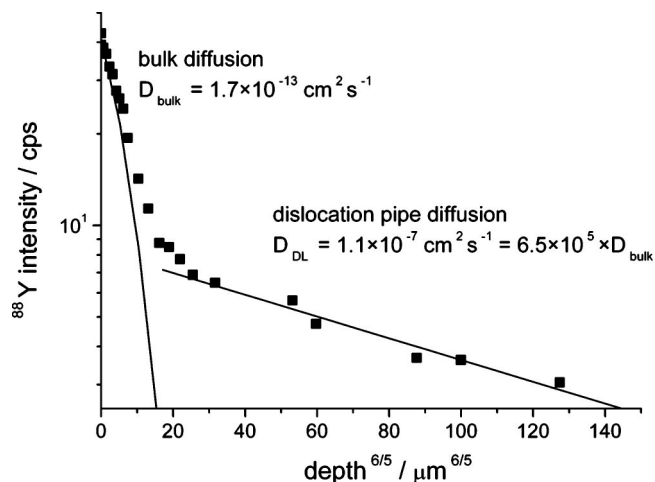


FIG. 1. Penetration profile [plotted according to Eq. (2)] for  $^{88}\text{Y}$  in YSZ containing 11.1 mol %  $\text{Y}_2\text{O}_3$  after heating for 72 h at 1598 °C. Also shown are the results of fits according to Eqs. (1) and (2) in the near-surface region and at large penetration depths.

$6 \times 10^{15} \text{ Zr}^+/\text{cm}^2$  using natural zirconium metal as a source. After implantation, the samples were heated for appropriate times at temperatures between 1070 and 1700 °C. Similarly,  $^{44}\text{Ca}$  (2.09% natural abundance) and  $^{90}\text{Zr}$  were implanted into CSZ containing 11.4 and 16.8 mol % CaO (obtained from Hrand Djvahirdjian S.A., Monthey/Switzerland; later referred to as CSZ-11 and CSZ-17, respectively). In this system, the Ca tracer diffusion was investigated in the temperature range from 960 to 1700 °C. The relative concentrations of the respective isotopes were monitored as a function of depth using SIMS. For further details on the experimental procedure, see Refs. 4 and 16.

### B. Radiotracer experiments

For  $^{88}\text{Y}$  diffusion, the isotope  $^{88}\text{Y}$  ( $t_{1/2} = 106.6 \text{ d}$ ; electron capture (EC) > 99%;  $\beta^+ 0.21\%$ ;  $E = 1.84 \text{ MeV}$ ) was applied from aqueous solution onto samples of YSZ containing 10.2, 11.1, 18.6, and 24.0 mol %  $\text{Y}_2\text{O}_3$  (later referred to as YSZ-10, YSZ-11, YSZ-18, and YSZ-24, respectively), dried and heated at 1400 to 1676 °C in air. After cooling down, two procedures according to the residual activity method have been applied in order to obtain the depth profile: In the first case, the sample height was monitored using a mechanical profiler, its residual radioactivity was measured (Ge:Li detector/multichannel analyzer, line at 1.84 MeV), and a small amount of the sample was removed by repeated polishing with SiC papers of 4000 down to 800 in.<sup>-2</sup> grit size. In the second case, the sample was weighed (Sartorius SC2) and its radioactivity was measured (NaI detector/multichannel INEL analyzer) before the next layer of the sample was removed (diamond polishing, 0.1 to 3  $\mu\text{m}$  particle size). The weight loss was converted into depth using the density of YSZ (6.0  $\text{g cm}^{-3}$ ). These procedures were repeated roughly 30 to 40 times and finally penetration profiles like that given in Fig. 1 were obtained. For more details on the radiotracer sectioning technique, see Refs. 17 and 18.

In Fig. 1, two regions can be distinguished. The steep falloff of the activity very close to the surface can be as-

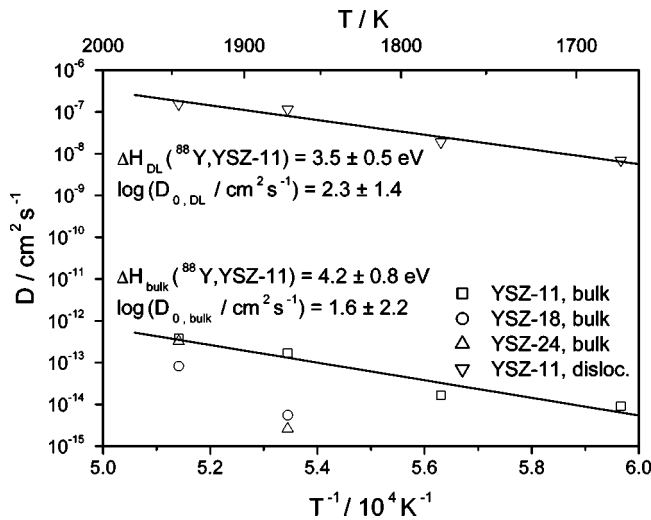


FIG. 2. <sup>88</sup>Y bulk and dislocation diffusion in YSZ containing 11, 18, and 24 mol % Y<sub>2</sub>O<sub>3</sub>.

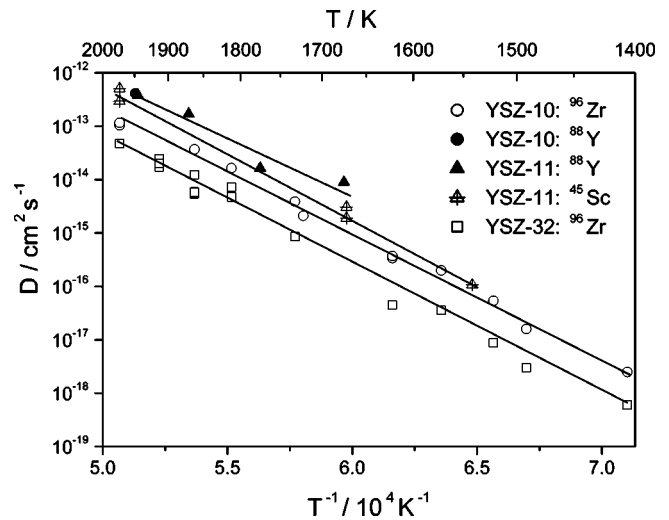


FIG. 3. Temperature dependence of the Y, Sc, and Zr bulk tracer diffusion in YSZ. The results of the Arrhenius fits are summarized in Table I.

signed to the bulk diffusion process. At a penetration depth beyond 20 μm<sup>6/5</sup> (≈ 12 μm), the decrease is less fast, suggesting dislocation pipe diffusion. In order to calculate diffusion coefficients, appropriate solutions of Fick’s equation were applied. For calculating the bulk diffusion coefficient  $D_{\text{bulk}}$ , Eq. (1) (taken from Ref. 19, p. 86) was used:

$$\frac{\Delta c(x,t)}{c(0,t)} = \exp\left(\frac{-x^2}{4D_{\text{bulk}}t}\right). \quad (1)$$

For calculating the dislocation diffusion coefficient  $D_{\text{DL}}$ , Eq. (2) was used (assuming a dislocation network:<sup>20</sup>)

$$\delta \times D_{\text{DL}} = 1.322 \left(\frac{D_{\text{bulk}}}{t}\right)^{1/2} \lambda^{-5/3}$$

with  $\lambda \equiv -\frac{\partial[\ln(c-c_\infty)]}{\partial x^{6/5}}.$  (2)

Here  $\Delta c(x,t) = c(x,t) - c_\infty$ , where  $c_\infty$  is the natural abundance of the tracer isotope ( $c_\infty = 0$  in the case of <sup>88</sup>Y),  $x$  is the penetration depth, and  $t$  the diffusion time. The dislocation width  $\delta$  was assumed to be 3 Å.

### III. RESULTS AND DISCUSSION

#### A. Yttrium tracer diffusion in YSZ

Yttrium bulk and dislocation diffusivities are given in Fig. 2. It can be seen that the dislocation diffusion is much faster and that it has a slightly lower activation enthalpy than the bulk diffusion (3.5 instead of 4.2 eV). It should be noted that the dislocation diffusion of yttrium is faster than the bulk diffusion by a factor of 10<sup>6</sup>. Extrapolating our results to 2000 °C, the difference between  $D_{\text{bulk}}$  and  $D_{\text{DL}}$  should be the same as found by Rhodes and Carter for polycrystalline CSZ around 2000 °C,<sup>14</sup> that is, a factor of 10<sup>5</sup>. Unfortunately, at the moment, no data concerning Zr dislocation or grain boundary diffusion in YSZ are available for comparison to our results. Waller *et al.* looked at the diffusion of manganese in YSZ (Mn assumed to be originally Mn<sup>3+</sup>), and found

a higher activation enthalpy for the grain boundary diffusion of this element than for bulk diffusion,<sup>12</sup> which is in contrast to our present findings. The authors explained this effect by a change of the oxidation state of manganese during the annealing and that the diffusivities should be a function of the oxidation state. Since the oxidation state of yttrium (Y<sup>3+</sup>) can be assumed to be stable, there should be no such influence in our experiments. Normally, one finds  $D_{\text{bulk}} < D_{\text{DL}} < D_{\text{GB}}$ , and  $\Delta H(D_{\text{bulk}}) > \Delta H(D_{\text{DL}}) > \Delta H(D_{\text{GB}})$ ,<sup>21</sup> meaning that the cation self-diffusion of yttrium in grain boundaries in YSZ should have activation enthalpies lower than 3.5 eV, while being at least six orders in magnitude faster than the bulk self-diffusion (in the temperature range investigated here).

#### B. Bulk diffusion in YSZ

The temperature dependencies of the bulk diffusion coefficients of Zr, Y, and Sc (scandium is considered to be similar to yttrium, taken from Ref. 8) in YSZ are shown in Fig. 3. It can be seen that the Zr diffusion is faster for YSZ-10 than for YSZ-32, which indicates a diffusion mechanism for Zr diffusion involving free vacancies  $V_{\text{Zr}}^{4'}$ , as proposed earlier.<sup>4</sup> This trend was also found for Y diffusion above and therefore, the diffusion via complex vacancies [e.g., formed according to Eq. (3)] is not very likely:



Furthermore, the diffusion of the lower charged cations Sc<sup>3+</sup> and Y<sup>3+</sup> is also faster than the Zr diffusion in YSZ: The diffusion coefficient of Y is about four times higher than the corresponding value for Zr (between 1400 and 1676 °C). The Sc diffusivity is only twice that of Zr. Solmon *et al.*<sup>3</sup> observed that in YSZ, the stabilizer ions moved faster than the host cations by a factor of 2.5, which is slightly smaller than the value observed here, probably due to the fact that Solmon measured chemical diffusion. The activation enthalpies and pre-exponential factors are summarized in Table I.

TABLE I. Ionic radii of cations in YSZ and CSZ in octahedral coordination (coordination number CN=8, from Ref. 22), relative cation diffusion coefficient, normalized to the corresponding Zr diffusion coefficients (averaged over the temperature range of measurement), activation enthalpies  $z_i/r_i^2$  (being proportional to the ionic “field strength”), and cation mass.

Ion I	Octahedral ion radius $r_i$ [pm]	Normal diffusion coefficient	Activation enthalpy $\Delta H$ [eV]	Pre-exponential factor $D_0$ [ $\text{cm}^2 \text{s}^{-1}$ ]	Temperature range [°C]	$z_i/r_i^2$ [ $\text{pm}^{-2}$ ]	Atomic mass [amu]
Zr <sup>4+</sup>	84	1	YSZ: 4.5 CSZ: 5.3	YSZ: 0.041 CSZ: 25	1070–1700 1120–1700	$5.7 \times 10^{-4}$	91.2
Sc <sup>3+</sup> (YSZ)	87	1.8	4.9	1.7	1270–1700	$4.0 \times 10^{-4}$	45.0
Y <sup>3+</sup> (YSZ)	101.9	4.3	4.2	0.024	1400–1676	$2.9 \times 10^{-4}$	88.9
Ca <sup>2+</sup> (CSZ)	112	5.5	5.1	45	960–1700	$1.6 \times 10^{-4}$	40.1

### C. Bulk diffusion in CSZ

Bulk diffusion coefficients obtained in CSZ are shown in Fig. 4. Here, Ca and Zr exhibited an Arrhenius behavior with practically identical activation enthalpies (5.14 and 5.29 eV), but Ca is faster than Zr by a factor of 5.5 (averaged over the measurement range). There is no evidence for a stabilizer concentration dependency of the cation diffusion (neither Zr nor Ca) in the range of 11 to 17 mol% CaO. Using simple defect chemistry, this finding was previously attributed to a cation transport process occurring via neutral vacancy complexes of the type  $[\text{V}_{\text{Zr}}^{4'} - 2\text{V}_{\text{O}}^{2'}]^x$ ,<sup>16</sup> which nevertheless cannot be observed experimentally. The activation enthalpy for diffusion of cations out of such complexes should therefore include an additional enthalpy of formation term. It should be noted that the cation (calcium) bulk diffusion obeys a linear Arrhenius behavior down to the lowest measurement temperature of 960 °C, where the bulk diffusion coefficient is as low as  $10^{-20} \text{cm}^2 \text{s}^{-1}$ , so that anneal times of nearly one year had to be used in order to see any diffusion effect in the SIMS depth profile.

### D. Comparison of bulk diffusion data

In order to understand the order of the cation diffusivities, some potentially interesting properties of the cations are summarized in Table I and shown in Fig. 6. Assuming that,

in stabilized zirconia, cations and oxygen vacancies are ideally distributed within the cubic lattice, one might expect that the difference in cation diffusivities be only affected by the mass difference of the ions.<sup>19</sup> In stabilized zirconia, the “light” elements Ca and Sc show different behaviors with respect to each other, as well as to the “heavy” elements Y and Zr. Thus, the masses of the cations are not solely responsible for the difference in the diffusion coefficients. An influence of the cation charge only can be ruled out as well since the fastest ion (calcium) has the highest negative excess charge on a zirconium site. Therefore, this negative electrical field around  $\text{Ca}_{\text{Zr}}^{2'}$  would repel the similarly negatively charged cation vacancy  $\text{V}_{\text{Zr}}^{4'}$  and should therefore decrease the cation diffusivity.

The size mismatch between Zr<sup>4+</sup> and the stabilizer ions decreases in the order  $\text{Ca}^{2+} > \text{Y}^{3+} > \text{Sc}^{3+}$ . The difference between the diffusion coefficients of zirconium and the other cations decreases in the same direction (see also Fig. 6). This suggests that the substitution of one ion by another of different size might cause a mechanical stress in the material enhancing cation diffusion. Kirkaldy *et al.*<sup>23</sup> have observed this effect when investigating the interdiffusion in binary alloys. They claimed that large atoms enhanced the diffusion by producing and collecting vacancies in their local neighbor-

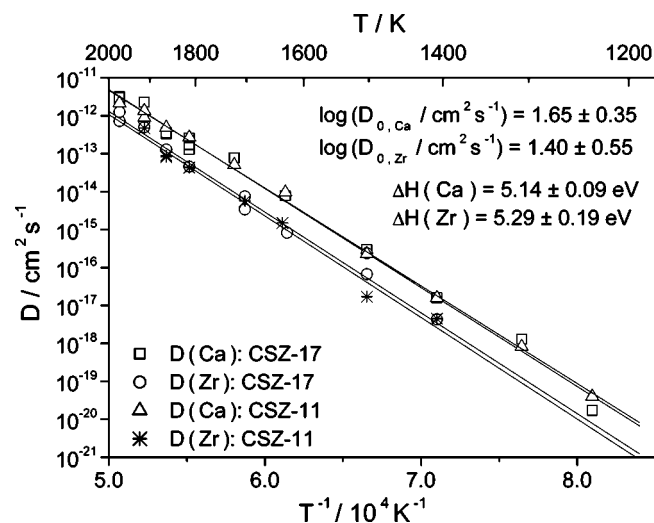


FIG. 4. <sup>44</sup>Ca and <sup>96</sup>Zr bulk diffusion in CSZ. Results of two joint fits of Ca and Zr diffusivities for both samples are also shown.

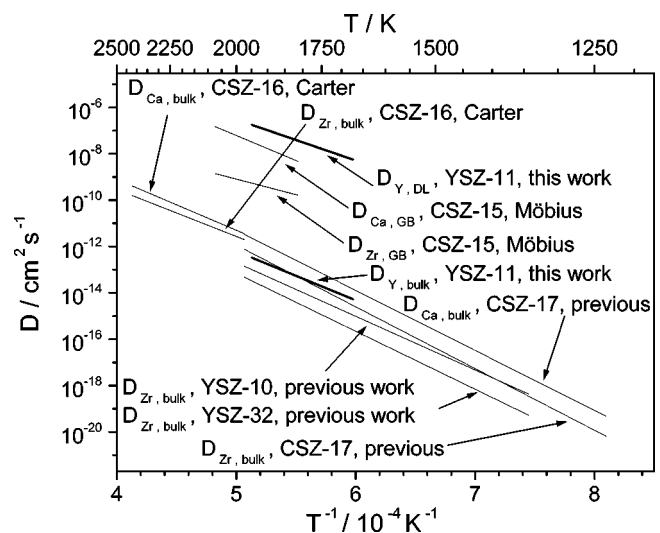


FIG. 5. Selected bulk and dislocation or grain boundary cation diffusion in CSZ and YSZ. Data are taken from: Carter (Ref. 14), Möbius (Ref. 15), and our previous work (Refs. 4 and 16).



hood. This should lead to a significant enhancement of the attempt frequency of diffusive jumps and consequently of the diffusion coefficient. It can be expected that this explanation holds true to some extent for ionic materials as well. Furthermore, there seems to be an inverse correlation of the ionic field strength, which is proportional to the charge of the migrating ion divided by the square of its radius, and the relative cation diffusion coefficients: The higher the charge density (the “harder” the cation), the lower the cation diffusion coefficients. Which of the discussed effects are actually responsible for the difference in cation diffusion coefficients is not yet clear. Combining the results of Kowalski *et al.*<sup>11</sup> for the bulk diffusion of the smaller  $\text{Ti}^{4+}$  with our data on  $\text{Zr}^{4+}$  diffusion, one finds that the  $\text{Ti}^{4+}$  diffusion is enhanced by a factor of 30 over the  $\text{Zr}^{4+}$  diffusion. As yet, it remains unclear whether the diffusion of smaller ions in YSZ occurs according to another diffusion mechanism than the diffusion of bigger ions or if the difference is simply due to experimental limitations.

Another aspect is how the different cation diffusion coefficients may influence kinetic demixing phenomena. This effect can occur when a system containing at least two different cations is exposed to any kind of external force: an electrical field,<sup>24</sup> an oxygen partial pressure gradient,<sup>25</sup> or a mechanical stress gradient.<sup>26</sup> Then, demixing towards the formation of pure oxides occurs according to the relative mobilities of the cations. It has been previously proposed that under the working conditions of a YSZ-based solid oxide fuel cells (SOFC), significant demixing should occur due to the different oxygen partial pressures for the case that the ratio of two cation diffusion coefficients is greater than 4/3.<sup>25</sup> If the oxygen partial pressures vary by a factor of  $10^7$  and the diffusivities differ by a factor of 2, the equilibrium concentration of the fastest cation at the high- $p\text{O}_2$  side is three times higher than at the low- $p\text{O}_2$  side of the YSZ electrolyte. This effect was confirmed experimentally in YSZ that was exposed to an external electrical field,<sup>24</sup> but the effect is only very small (less than 500 ppm variation in yttria content).

According to our experimental work reported here, we would expect kinetic demixing to occur in the SOFC, since we have found that yttrium moves four times faster than zirconium in the YSZ bulk. Using transmission electron microscopy on well-defined bicrystals, Lei *et al.*<sup>27</sup> were also able to show that yttrium segregates to the boundary between the two YSZ crystals, suggesting that the element is likely to segregate at grain boundaries, which can be understood using the results obtained here. Nevertheless, the currently discussed operation temperatures of the SOFC (800 up to 950 °C) are very low in comparison to the cation diffusion measurement temperatures used here. Therefore, any chemical decomposition of the material should happen relatively slowly; even at 950 °C, the bulk diffusion coefficients of either Zr or Y would be lower than  $10^{-19} \text{ cm}^2 \text{ s}^{-1}$ , and at 800 °C, the cation diffusion would be furthermore much decreased.

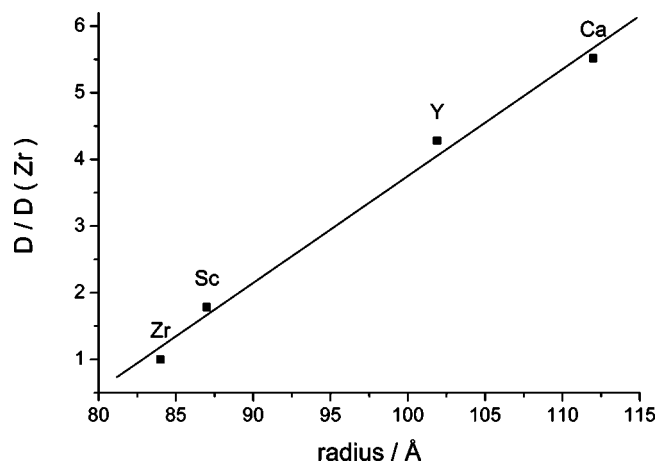


FIG. 6. Comparison of relative cation diffusion coefficients in YSZ and CSZ. Data are taken from Table I. The line is drawn as a guide only.

### E. Comparison of dislocation and grain boundary diffusion data

Bulk and grain boundary diffusion data are compared to literature values in Fig. 5. In CSZ, Rhodes and Carter<sup>14</sup> have measured the bulk and grain boundary diffusion of the two constituent cations in the temperature range 1700 to 2150 °C. They estimated the grain boundary diffusion coefficient to be  $10^4$ – $10^5$  times faster than the bulk diffusion, and calcium is roughly 10 times faster than Zr. The activation enthalpies for grain boundary diffusion should be not too different from the bulk value. In another work, Möbius *et al.*<sup>13</sup> investigated scandia- and calcia-stabilized zirconia (ScSZ). Their calcium grain boundary diffusion coefficients (despite originally claimed to be bulk diffusion coefficients) are about  $10^5$  times higher than the bulk diffusion coefficients measured by Rhodes and Carter. However, it is remarkable that their zirconium grain boundary diffusion coefficients are well below the calcium grain boundary diffusion coefficients (about three orders of magnitude), also with a lower activation enthalpy of the calcium grain boundary diffusion. The bulk diffusion coefficients of Ca and Zr, as mentioned earlier, are much less different from each other. If the results in Ref. 13 were correct, different diffusion mechanisms for the two cations would exist in the grain boundary. The dislocation diffusivities measured by us are relatively high in comparison to the bulk diffusivities observed, but unfortunately, there are no data as yet on dislocation pipe diffusion of zirconium in single-crystalline YSZ available that would allow a comparison to our results.

In a previous work, we studied the grain boundary diffusion of Mn in YSZ and found that the grain boundary diffusion is also faster than the bulk diffusion.<sup>28</sup> Surprisingly, as also previously observed by Waller *et al.*,<sup>12</sup> the activation enthalpy for grain boundary migration is higher than for bulk diffusion. These results were explained as changes in the oxidation state of manganese during the experiment. Another possible explanation might be the formation of secondary intergranular phases. Recent stable tracer investigation of the Zr self-diffusion in polycrystalline ScSZ resulted in both bulk and grain boundary diffusion coefficients of Zr having

different activation enthalpies [ $\Delta H(D_{\text{bulk}})=5.0$  eV,  $\Delta H(D_{\text{GB}})=3.9$  eV,  $D_{\text{bulk}}/D_{\text{GB}}=10^{-6}-10^{-7}$ ].<sup>29</sup> According to Kowalski, the grain boundary diffusion of  $\text{Ti}^{4+}$  (0.74 Å, and therefore even smaller than  $\text{Zr}^{4+}$ ) and  $\text{Ca}^{2+}$  into YSZ show significantly different behavior, it is much faster for  $\text{Ca}^{2+}$ . For  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$ , which are chemically similar and have lower charges but have significantly different ionic radii (0.89 and 1.12 Å), Bak *et al.*<sup>10</sup> found a very big difference for the bulk and grain boundary diffusion into YSZ. It seems, at least according to the recent results on tracer diffusion in YSZ, that cation grain boundary diffusion might be dominated by charge effects while, according to our results on self-diffusion in YSZ and CSZ, the cation bulk diffusion is mainly ruled by ionic size effects. Similar results were also obtained when performing model calculations on the cation migration in perfect  $\text{ZrO}_2$ , where it was shown that the migration energy of diffusion is a function of both the ionic radius and ionic charge.<sup>30</sup> To support this finding, further experimental work using direct methods like stable and radiotracer diffusion is necessary.

#### IV. CONCLUSIONS

Yttrium tracer diffusion in YSZ was measured directly by using the radiotracer  $^{88}\text{Y}$ , and both bulk and dislocation diffusivities were obtained from the resulting profiles. The following results are deduced.

- (1) Yttrium self-diffusion is four times faster than Zr self-diffusion. The activation enthalpy (4.2 eV for YSZ containing 11 mol%  $\text{Y}_2\text{O}_3$ ) is slightly lower than the respective value of the zirconium diffusion.
- (2) In the investigated temperature range (1400–1676 °C) dislocation pipe diffusion of yttrium in YSZ is about six orders of magnitude faster than bulk diffusion and has a lower activation enthalpy (3.5 eV for YSZ containing 11 mol%  $\text{Y}_2\text{O}_3$ ). Extrapolating this behavior, dislocation pipe diffusion will become even more dominant at low temperatures.
- (3) The yttrium bulk diffusion coefficient decreases with increasing yttrium content, similar to the observation made for zirconium self-diffusion, indicating that cation transport occurs via single vacancies.
- (4) Both for YSZ and CSZ, the diffusion coefficient of zirconium has the lowest values, being therefore rate determining for effects such as mechanical creep. The difference in cation diffusion coefficient is tentatively assigned to be proportional to the ionic radius of the migrating ion.

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