LANTHANIDE DIFFUSION IN CALCIA STABILIZED ZIRCONIA: EXPERIMENTAL AND THEORETICAL STUDY

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ABSTRACT

Multiple diffusion experiments of all stable lanthanides were performed simultaneously in calcia-stabilized zirconia (CSZ) in the temperature range between 1286° and 1463°C. The bulk diffusion coefficient obtained increases with increasing ionic radius. The experimental activation enthalpy is near 6 eV and is not strongly affected by the type of lanthanide. These results were correlated with calculations of the cation diffusion using the Mott-Littleton-approach. An association energy of cation vacancies with oxygen vacancies of about 1 eV was deduced.

INTRODUCTION

The degradation process in ZrO2-based ceramics is believed to be governed by the slow diffusion of cations and in particular related with the size mismatch between the stabilizer and host cations as was proposed for yttria stabilized zirconia (YSZ) (1). There is recently an increased interest in measuring and calculating the cation diffusion in this material. In previous work, we investigated the diffusion of constituent cations both in yttria- and calcia-stabilized zirconia using single crystalline material (2, 3). The diffusion of foreign cations was investigated in Bal et al. (4), who looked at Mg diffusion in YSZ, and by Kowalski et al., who looked at the diffusion of Ca and Ti in YSZ (5,6). For the bulk self-diffusion of the constituent cations, we found activation energies of 4.5-5.0 eV in YSZ and 5.0-5.5 eV in CSZ. The stabilizer elements are faster than the host cation by a factor of 3-7. The Mg and Ca diffusion in YSZ showed a much smaller activation energy of 4.0 and 3.4 eV, while Ti has an activation energy of 5.2 eV.

A general explanation of the cation migration process in stabilized zirconias (both diffusion coefficient and activation energy) is still missing. It is generally believed that migration goes via Schottky vacancies, but details such as the state of the vacancies (free or associated) are still unknown. A first approach to clear up the effect of ionic radius on

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the cation diffusion in YSZ was done when the multi-diffusion of lanthanides in YSZ was investigated (1). In this work we observed that the diffusion coefficient is a function of the ionic radius and increases when it is close to the radius of the host cations. The idea of the present multiple diffusion experiment is to take lanthanides as a probe for cation diffusion because they are chemically similar to zirconium and show a very small change in physical-chemical properties, but their ionic radius is changing. After allowing them to diffuse into a sample, the depth distribution of lanthanides is measured using secondary ion mass spectroscopy (SIMS). This method is experimentally complicated, and therefore, many errors might be introduced during preparation, annealing, and analysis of different samples. Since the differences in the diffusion coefficients are expected to be only small, it is necessary to perform a multiple diffusion study of all lanthanides in parallel in order to minimize experimental errors.

The experimental results are explained using theoretical calculations of the cation migration enthalpy in cubic zirconia. There is not very much work done on modelling the cation diffusion in zirconia. Values of 8.5 eV are reported by Mackrodt et al. for the migration energy of zirconium (7). We used the Mott-Littleton-approach (8) to look at the cation diffusion energy as well as at the diffusion mechanism.

**EXPERIMENTAL RESULTS**

A 16.8 mol% CSZ single crystal was cut into slabs, polished, and heated at 1400°C for one week before doping. An ICP lanthanide standard solution (containing all stable lanthanides as well as zirconium, yttrium, and scandium: Alfa #23261; 100 µg/ml each in 5% HNO₃) was diluted (1:20 with a 1:1 water/ethanol mixture) and dropped onto the surface of the crystals. The layer thickness was estimated to be in the range of 10 to 20 nm. For diffusion experiments, the dried samples were heated in air at 1286°C, 1376°C and 1463°C for 10 days, 3 days, and 1 day, respectively.

The depth distribution of the cations was analyzed using two different SIMS machines (VG SIMS lab and Cameca IMS 3f). Ar⁺ or O⁺ ions (7 kV, 100 to 320 nA) were scanned over an area of up to 250x250 µm². Charge compensation was performed either by using an electron flood gun or by covering the surface with a thin layer of carbon. The sputter profiles were converted into depth by measuring the crater depth with a surface profiler. Typical diffusion profiles after heating at 1376 °C for 3 days are shown in Figure 1.

To get the diffusion coefficients, the SIMS measurements were analyzed as a function of depth using the intensity ratios \( \frac{I_{\text{Ln}}}{I_{\text{Zr}}} \) according to equation [1] (9).

\[
C = \frac{C_0}{2} \left[ \text{erf} \left( \frac{h-x}{2\sqrt{D}t} \right) + \text{erf} \left( \frac{h+x}{2\sqrt{D}t} \right) \right]
\]

[1]

Here, \( h \) is the initial layer thickness (10–20 nm), and \( C_0 \) the initial relative concentration of the respective lanthanide. Figure 2 represents the bulk diffusion coefficients dependence as a function of lanthanide ionic radii. An 8-fold coordination was assumed (according to the expected fluorite structure) (10).

It can be seen that the diffusion coefficient is constant for ionic radius below 1.0 Å and increases by a factor of 3–5 to remain constant above 1.1 Å. The lower value is similar to that of the zirconium self-diffusion; the higher values those of calcium self-diffusion.
An activation enthalpy near 6 eV was determined for all lanthanides from an Arrhenius plot (Figure 3). The values were higher than those obtained for the lanthanide diffusion in YSZ (1) but still do not show a significant correlation to the lanthanide type. In the case of Sc$^{3+}$, which is even slightly smaller than the host cation Zr$^{4+}$, the activation enthalpy was lower (4.3 ± 0.8 eV) and closer to the value found for zirconium self diffusion in CSZ (5.1±0.3 eV) (2).
Figure 3. Arrhenius plot of tracer diffusion of dysprosium in CSZ. The line represents a fit giving an activation energy of 6.1 eV and a pre-exponential factor of $8 \times 10^{-3} \text{ m}^2 \text{s}^{-1}$.

The pre-exponential values are in the range of $10^1$ to $10^{12} \text{ m}^2 \text{s}^{-1}$, corresponding to an activation entropy of diffusion $\Delta S$ in the range of 10 to 20 k$_{\text{B}}$, calculated according to (1). This value is higher than that determined for YSZ. In the literature, it is shown that a diffusion mechanism going via free vacancies should result in an activation entropy of 3 k$_{\text{B}}$ for formation and 3 k$_{\text{B}}$ for migration of simple defects (11), resulting in a total value no greater than 6 k$_{\text{B}}$. Because our values are significantly higher, the underlying atomistic mechanism must be more complex. This is supported by our previous self-diffusion experiments (4), where it was deduced that the migration in CSZ should go via electrically neutral complex vacancies consisting of one cation vacancy associated with two oxygen vacancies, $[\text{V}_z^4,2\text{V}_o^2]^x$.

COMPUTER SIMULATION RESULTS

To clear up the effect of the lanthanides on the cation diffusion, computer simulations using the Mott-Littleton-Approach were performed. With this method, the migration energy for ionic migration can be modeled in perfect cubic ZrO$_2$. For comparison, two different potential sets were used. The first was developed by Jackson when modeling lanthanide halides (12), and the second by Grimes for pyrochlore compounds and doped cerium oxides (13). The potentials for ZrO$_2$ were taken previously from Cormack (14) and optimized to cubic ZrO$_2$ (15).

To model cation migration, two cation vacancies were created in perfect cubic ZrO$_2$ containing no defects at adjacent cation sites. Then, one lanthanide cation was placed at different positions between these vacancies and the surrounding was allowed to relax. The configuration energies are calculated and plotted as a function of lanthanide position. From this plot, the migration pathway can be deduced, which is for all lanthanides and all potential sets nonlinear (see Figure 4). For comparison, the migration of the host cation Zr$^{4+}$ was also modeled. The migration energies are defined as the saddle-point energies.
Figure 4. Zr$^{4+}$ migration in perfect cubic zirconia. The initial crystallographic positions of the two cation vacancies are (0,0,0) and (1/2,1/2,0). One Zr$^{4+}$ ion is then placed over the whole range with $z = 0$.

The resulting migration energies are shown for all lanthanides and the two potential sets in Figure 5 as a function of the lanthanide ionic radii adapted from Shannon (10).

As can be seen in Figure 5, the migration enthalpy is between 3.5 and 5.5 eV. The values obtained using Grimes' potential set (13), developed for CeO$_2$, show only a small ionic radius dependency; the migration energy is slightly decreasing from 4.7 to 4.3 eV when increasing the ionic radius. With Jackson's potential set (12), the migration energy is more strongly dependent and increases from 3.5 to 5.2 eV with increasing ionic radius.

Figure 5. Computer simulation of cation migration in cubic zirconia using parameter sets of Jackson (circles) (12) and Grimes (triangles) (13).
Nevertheless, the radius dependency of the migration energy is in both cases not leading to a straight line, but there is a stronger dependency in the range of 1.00 to 1.05 Å. This corresponds to the range where the experimental measured cation diffusion showed a strong change.

**DISCUSSION**

The connection between experimental and simulation results can be done by comparing the activation energies. The experiment values for lanthanide diffusion are around 6.0 eV, without a significant dependency on the lanthanide type, while the calculated values are significantly lower. With the Grimes model, a mean value of 4.5 eV was found with only a small dependency of the lanthanide ionic radius, while the Jackson values range from 3.5 to 5.2 eV, but also centered around 4.5 eV. Although the Jackson potential set is more complete and reliable, the Grimes potential set is developed for lanthanide doped ceria and pyrochlores, which are more similar to the investigated system than the lanthanum halides used for developing the Jackson potentials. Therefore, for comparing the experimental and calculated activation energies we focus on the results of the Grimes calculation. The difference between these values is then 1.5 eV, roughly constant for all lanthanides. From the self-diffusion studies in CSZ it was concluded that the migration goes via complex defects \([V_{Zr}^{4},2V_{O}^{2+}]^{x}\), and the experimental activation energy should be a sum of the migration energy, a formation and an association term (2). The calculated values are the pure migration energy, and therefore the difference of 1.5 eV can be attributed to the formation of defect associates.

In YSZ, the activation energies for lanthanide diffusion were smaller by 1 eV than the values observed for CSZ (1). Similarly, the self-diffusion of the host cations was between 4 and 5 eV (16), also up to 1 eV smaller than found for the host cations in CSZ (2). It was concluded that in YSZ the cation diffusion goes via free vacancies. The difference between the two systems CSZ and YSZ of 1 eV is consistent with the explanation given here that only in CSZ the measured activation enthalpy contains an extra contribution due to defect association.

When comparing the experimental and calculated values for the migration energy, a change in the ionic radius-dependency of the evaluated parameters around 1.0 Å was observed in both cases: Below this value, the diffusion coefficient is constant and then increases by a factor of 3-5. A previous experimental study on the lanthanide diffusion in YSZ gave the same result (1) indicating that there is a similar diffusion mechanism in both systems. Also, the calculated activation energies are constant below 1.0 Å and then change slightly for both potential sets investigated here. Therefore, a migrating cation in cubic zirconia seems to be identically affected by its local surrounding when it is smaller than 1.0 Å. For bigger cations, the interaction is gradually modified, leading to the slight changes observed here both experimentally and from the modeling. Regarding the diffusion of Sc\(^{3+}\), which is even slightly smaller than Zr\(^{4+}\), we found significantly lower values than for both the lanthanides and the host self diffusion. That means that the scandium diffusion in CSZ seems to be governed by another type of transport process, probably by migration via non-associated defects.

Kowalski et al. (5,6) found that the bulk diffusion coefficients for the bigger ion Ca\(^{2+}\) are higher than for the smaller Ti\(^{4+}\), as observed in the self diffusion study earlier (2). Here,
we investigated lanthanides that can be considered to be mainly three-fold charged and found the same behavior, namely, that smaller cations have a lower cation diffusion coefficient than bigger ones. This fact could be an indication that different mechanisms are involved in the diffusion of cations smaller than the stabilizer ions even if the charge of the ion is different. It seems that the ionic radius is a more relevant parameter than the ionic charge for controlling the cation diffusion process. More work, both experimentally and theoretically, is in progress to give a better insight in this problem.

CONCLUSIONS

The diffusion of lanthanides was studied experimentally in single crystalline CSZ between 1286° and 1463°C. Lanthanide migration energies were calculated using the Mott-Littleton approach. The following key results were obtained:

- The bulk diffusion coefficient is dependent on the ionic radius of the lanthanide tracer. For radii lower than 1 Å, it is constant and roughly identical to the zirconium self-diffusion coefficient, while for higher ionic radii, the diffusion coefficient approaches the stabilizer value.

- The experimental activation enthalpies are about 6 eV, almost constant for all lanthanides. The Mott-Littleton calculations results in 1.5 eV smaller values, also nearly constant. The difference can be explained with defect association.

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REFERENCES

1. S. Weber, S. Scherrer, H. Scherrer, M. Kilo, M.A. Taylor, and G. Borchardt, Applied Surface Science, in press (2002).
2. M. Kilo, G. Borchardt, S. Weber, S. Scherrer, K. Tinschert, B. Lesage, and O. Kaftasov, Rad. Eff. Defect Solids, 151, 29 (1999).
3. M. Kilo, G. Borchardt, R.A. de Souza, E. Ivers-Tiffée, S. Weber, and S. Scherrerr, Solid-State Ionic Devices, E. D. Wachsman et al. editors, PV 99-13, p. 228, The Electrochemical Society Proceedings Series, Pennington, New Jersey (1999).
4. C. T. Bak, J. Nowotny, K. Prince, M. Rekas, and C. C. Sorrell, J. Am. Ceram. Soc., 85, 2244 (2000).
5. K. Kowalski, A. Bernasik, and A. Sadowski, J. Europ. Ceram. Soc., 20, 2095 (2000).
6. K. Kowalski, A. Bernasik, and A. Sadowski, J. Europ. Ceram. Soc., 20, 951 (2000).
7. W. C. Mackrodt and P. M. Woodrow, J. Am. Ceram. Soc., 69, 277 (1986).
8. N. F. Mott and M. J. Littleton, *Trans. Faraday Soc.*, 34, 485 (1938).

9. Y. M. Chiang, D. P. Birmie, and W. D. Kingery, *Physical Ceramics*, p. 188, J. Wiley & Sons, New York (1997).

10. R. D. Shannon, *Acta Cryst.*, A32, 751 (1970).

11. J. Philibert, *Atomic Movements in Solids*, pp. 86, 99, Les Editions de Physique, Les Ulis (1991).

12. M. E. Valerio, R. A. Jackson, and J. F. de Lima, *J. Phys. Condens. Matter*, 12, 7727 (2000).

13. L. Minervini, R. W. Grimes, and K. E. Sickafus, *J. Am. Ceram. Soc.*, 83, 1873 (2000).

14. A. Dwivedi and A. N. Cormack, *Philos. Mag.*, A61, 1 (1990).

15. M. Kilo, C. Fundenberger, C. Argirusis, G. Borchardt, R. A. Jackson, and M. Weller, *Rad. Eff. Defect Solids*, in press.

16. M. Kilo, G. Borchardt, B. Lesage, S. Weber, S. Scherrer, M. Martin, and M. Schroeder, *Solid Oxide Fuel Cells VII*, H. Yokokawa and S. C. Singhal, Eds., PV 2001-16, p. 275, The Electrochemical Society Proceedings Series, Pennington, New Jersey, (2001).