

Lanthanide transport in stabilized zirconias: Interrelation between ionic radius and diffusion coefficient

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The diffusion of all stable lanthanides was measured both in calcia stabilized zirconia (CSZ) and in yttria stabilized zirconia (YSZ) in the temperature range between 1286 and 1600 °C. The lanthanide diffusion coefficients obtained increase with increasing ionic radius. The experimental activation enthalpy of diffusion is near 6 eV for CSZ and between 4 and 5 eV for YSZ and is not strongly affected by the type of lanthanide. The results were correlated with defect energy calculations of the lanthanide diffusion enthalpy using the Mott-Littleton approach. An association enthalpy of cation vacancies with oxygen vacancies of about 1 eV (96 kJ/mol) was deduced in the case of CSZ, while there is no association in the case of YSZ. Furthermore, the change in diffusion coefficients can be correlated to the interaction parameter for the interaction between the lanthanide oxide with zirconia: The higher the interaction parameter, the higher the lanthanide diffusion coefficient.

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I. INTRODUCTION

The surprisingly high ionic conduction in (yttrium or calcium) stabilized cubic zirconia (YSZ or CSZ) makes these materials useful as solid electrolytes in high temperature solid oxide fuel cells and for oxygen sensors. The conductivity is connected with the presence of oxygen vacancies, which are created as charge compensating defects. Nevertheless, the oxygen conductivity is not constant as a function of time: It decreases slowly and is reduced significantly after very long operation times. This 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 YSZ.¹

In recent years, there is an increased interest in measuring and calculating the cation diffusion in this material. In previous work, the diffusion of constituent cations was investigated both in yttria- and in calcia-stabilized zirconia using single crystalline materials.^{2,3} Two different groups recently investigated the diffusion of foreign cations in polycrystalline YSZ. Nowotny *et al.* studied Mg diffusion in YSZ,⁴ and Kowalski *et al.*^{5,6} investigated the diffusion of Ca and Ti in YSZ. Activation enthalpies for the bulk self-diffusion of the constituent cations were found to be in the range 4.5–5.0 eV in YSZ,² and 5.0–5.5 eV in CSZ.³ The stabilizer elements are faster than the host cation by a factor of 3–7. Mg²⁺ and Ca²⁺ diffusion in YSZ showed a much

smaller activation energy of 4.05 and 3.46 eV, respectively,^{4,5} while Ti⁴⁺ has a higher activation enthalpy of 5.24 eV.⁶

A general explanation of the cation migration process in stabilized zirconias (both diffusion coefficient and activation enthalpy) is still missing. It is commonly believed that migration proceeds via vacancies, but details like the state of the vacancies (free or associated with oxygen vacancies) are still unknown. A first approach to clarify the effect of ionic radius on the cation diffusion in YSZ was done in a previous work investigating the multicomponent diffusion of lanthanides in YSZ.¹ In this work it was observed that the diffusion coefficient is a function of the ionic radius and is increasing when close to the radius of the host cations.

To contribute to the understanding of the diffusion mechanism in stabilized zirconias, a multicomponent diffusion experiment on calcia and yttria stabilized zirconia is performed. Lanthanides constitute a good set of probes for studying the cation self-diffusion in YSZ and CSZ because they are chemically similar to zirconium and yttrium; they show a very small but gradual change in physicochemical properties and mainly their ionic radius varies.

The experimental results are explained using theoretical calculations of the lanthanide migration enthalpies in cubic zirconia using the Mott-Littleton method.⁷

II. EXPERIMENTAL RESULTS

A 16.8 mol % CSZ single crystal and a 11.1 mol % YSZ single crystal were cut into slabs, polished (final grain size: 0.5 μm) and then preannealed at 1400 °C for 7 days before doping. An inductively coupled plasma (ICP) lanthanide

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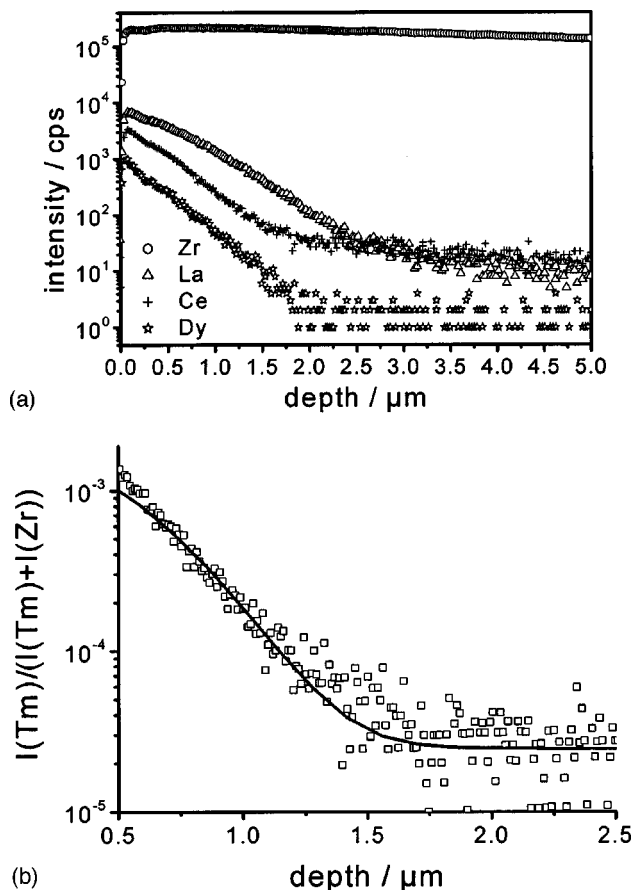


FIG. 1. Diffusion depth profiles of different lanthanides for the lanthanide doped CSZ specimen annealed at 1376 °C for 3 days. (a) Original SIMS depth profiles for the host element Zr and selected lanthanides La, Ce, and Dy. (b) Normalized spectrum $I(\text{Tm})/[I(\text{Tm})+I(\text{Zr})]$, together with the fit according to Eq. (1).

standard solution (containing all stable lanthanides as well as zirconium, yttrium, and scandium (Alfa Chemicals No. 23261; 100 $\mu\text{g}/\text{ml}$ each in 5% HNO_3) was diluted (1:20 with a 1:1 water/ethanol mixture) and dropped repeatedly onto the surface of the crystals. The solution was evaporated by heating to 60–80 °C after each step, until a thin lanthanide oxide layer with an approximate thickness in the range of 10–20 nm was obtained on top of the zirconia crystals, which were used as diffusion sources. For diffusion experiments, the dried samples were heated in air at 1286, 1376, and 1463 °C for 10 days, 3 days, and 1 day, respectively for CSZ. 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 $250 \times 250 \mu\text{m}^2$. Charge compensation was performed either by using an electron flood gun or by covering the surface with a thin carbon layer. The sputter profiles were converted into depth by measuring the crater depth with a surface profiler. Typical diffusion profiles for selected elements after heating at 1376 °C for 3 days are shown in Fig. 1.

To get the diffusion coefficients, the SIMS measurements were analyzed as a function of depth using the intensity ratios $[\text{Ln}/(\text{Ln}+^{96}\text{Zr})]$ according to Eq. (1).⁸

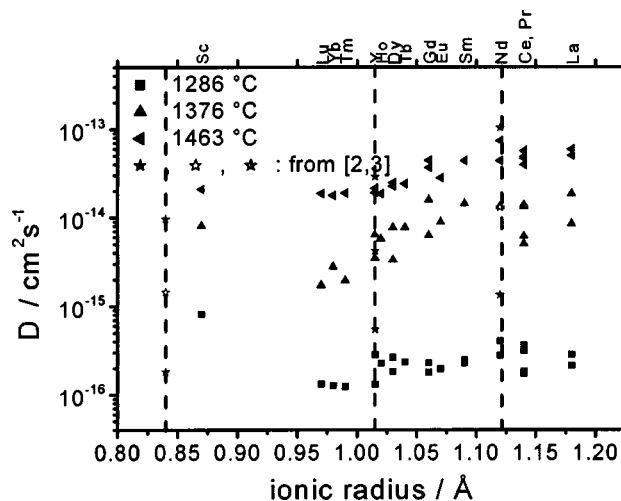


FIG. 2. Cation diffusion coefficients in CSZ for the different lanthanides, host cations, and scandium plotted as a function of their ionic radius. The lines indicate the stabilizer (Ca^{2+}) and host (Zr^{4+}) ionic radii. Values for the self-diffusion of Zr^{4+} and Ca^{2+} (stars) are taken from Ref. 2. The radii are according to Shannon (Ref. 9).

$$C = \frac{C_0}{2} \left[\operatorname{erf} \frac{h-x}{2\sqrt{Dt}} + \operatorname{erf} \frac{h+x}{2\sqrt{Dt}} \right]. \quad (1)$$

Here, h is the initial layer thickness (10–20 nm), and C_0 the initial relative concentration of the respective lanthanide. This equation fitted the results quite well, as can be seen from a comparison between the experimental and fitted profiles in Fig. 1.

Figure 2 represents the bulk lanthanide diffusion coefficients as a function of lanthanide ionic radii. An eight-fold coordination was assumed (according to the expected fluorite structure⁹) and all lanthanides were considered to be triply charged (in contrast to the assumptions made recently in Ref. 1). It can be seen that the diffusion coefficient is constant for ionic radii below 1.0 \AA and then increases by a factor of 3–5 to remain constant above 1.1 \AA . The lower value is similar to the value of the zirconium self-diffusion, the higher values are close to the values of calcium self-diffusion.

The same “step” behavior was observed when studying the lanthanide diffusion in YSZ. Figure 3 shows a comparison of CSZ and YSZ lanthanide diffusion for samples diffused at 1463 °C (CSZ) and 1700 °C (YSZ). In both systems, the lanthanide diffusion coefficient changes on approaching the stabilizer ion radius.

An activation enthalpy ΔH near 6 eV was determined for the diffusion of all lanthanides in CSZ from an Arrhenius plot according to Eq. (2) (Fig. 4). The values are higher than those obtained for the lanthanide diffusion in YSZ,¹ where values between 4 and 5 eV were found, but still do not show a significant correlation to the lanthanide type,

$$D = D_0 \exp\left(\frac{-\Delta H}{kT}\right). \quad (2)$$

In the case of Sc^{3+} , which is only slightly bigger 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-

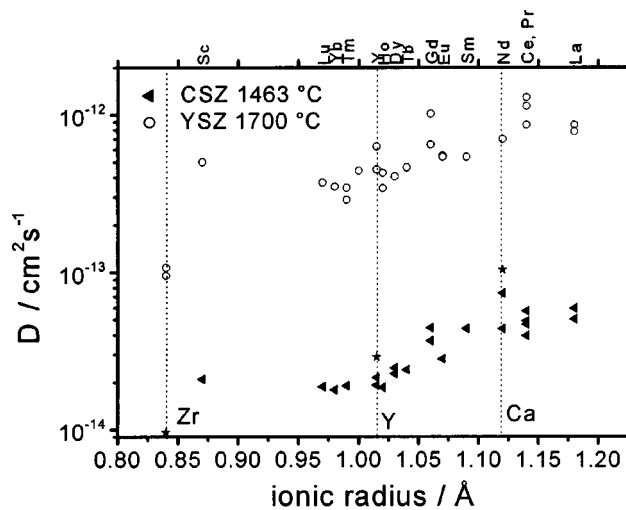


FIG. 3. Comparison of lanthanide diffusivities obtained in YSZ and CSZ. For better comparability, different temperatures were chosen. Stars indicate the self-diffusivities of host and dopant cations (taken from Refs. 2 and 3).

diffusion in CSZ (5.1 ± 0.3 eV).² All results are summarized in Table I together with similar results on lanthanide diffusion in YSZ.

The preexponential values obtained are in the range of $10^{-1} - 10^{+2}$ $\text{cm}^2 \text{s}^{-1}$, corresponding to an activation entropy of diffusion ΔS in the range of $(10-20)k_B$, calculated according to Weber *et al.*¹ These values are higher than determined for YSZ $(1.2-6)k_B$. In the literature, it is shown that diffusion via free vacancies should result in an activation entropy of $3k_B$ for formation and $3k_B$ for migration of simple defects,¹⁰ resulting in a total value not greater than $6k_B$. The relatively high values obtained here could indicate a more complex atomistic mechanism of cation diffusion, as discussed below. This feature was also observed in previous self-diffusion experiments,² where it was deduced that the migration in CSZ should occur via electrically neutral complex vacancies consisting of one cation vacancy associated with two oxygen vacancies, $[V_{\text{Zr}}^{4'}2V_{\text{O}}^{2\bullet}]^x$.

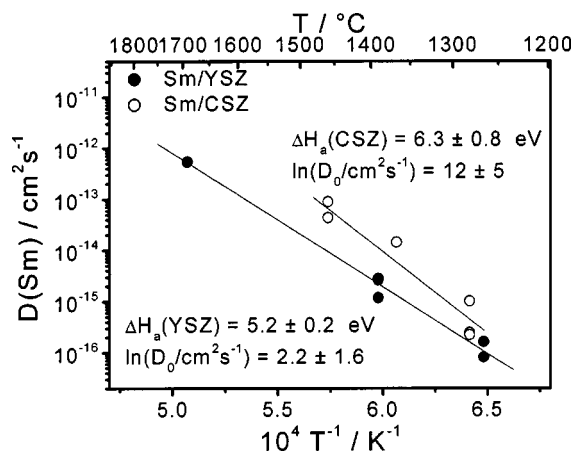


FIG. 4. Arrhenius plot of tracer diffusion of Samarium in CSZ (open circles) and YSZ (closed circles). The line represents a fit according to Eq. 2 giving the indicated values for the activation energy and preexponential factor.

III. COMPUTER SIMULATIONS RESULTS

Using the Mott-Littleton approach the migration enthalpy 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,¹¹ and the second by Grimes for pyrochlore compounds and doped cerium oxides.¹² The potentials for ZrO_2 were taken previously from Cormack¹³ and optimized to cubic ZrO_2 .¹⁴

To model the cation migration, two cation vacancies were created in perfect cubic ZrO_2 containing no other defects at adjacent cation sites. Then, one lanthanide cation was placed at different positions between these vacancies and the surrounding lattice was allowed to relax. The configuration enthalpies were calculated and plotted as a function of lanthanide position. From this plot, the migration pathway could be deduced, which is nonlinear for all lanthanides and all potential sets (see Fig. 5). For comparison, also the migration of the host cation Zr^{4+} was modeled. The migration enthalpies are defined as the saddle-point enthalpies. The resulting migration enthalpies are shown for all lanthanides and the two potential sets in Fig. 6 as a function of the lanthanide ionic radii taken from Shannon.⁹

As can be seen from Fig. 6, the migration enthalpy is between 3.5 and 5.5 eV. The values obtained using Grimes' potential set,¹² developed for CeO_2 , show only a small ionic radius dependency; the migration enthalpy is slightly decreasing from 4.7 to 4.3 eV when increasing the ionic radius. With Jackson's potential set (for halides),¹¹ the migration enthalpy is more strongly dependent and increases from 3.5 to 5.2 eV when increasing the ionic radius.

IV. DISCUSSION

The diffusion profiles of all cations in single crystalline CSZ and YSZ were monitored in parallel, i.e., a mixture of all lanthanides can be used as a probe system for measuring the cation diffusion in zirconia. This allows in principle a much better insight into the mechanism of the cation diffusion in stabilized zirconias (and even in similar materials) than the use of only one element in different experiments as has been recently done by Kowalski *et al.*^{5,6} Lanthanide oxides are known to form solid solutions with ZrO_2 similar to yttria and calcia, which should make them a good replacement for monitoring cation diffusion. Under the experimental conditions (20 nm initial layer thickness, some 100 nm diffusion length), it can be expected that the lanthanides are forming a dilute solution in zirconia, and in no case, the system will be above the stability limit of the cubic phase. Above this stability limit of 40–50 mol % stabilizer content, ordered phases are known to be formed in YSZ and in CSZ, e.g., being in the pyrochlore ($\text{La}_2\text{Zr}_2\text{O}_7$) structure or similar ones.

The values of the activation enthalpy of diffusion in CSZ are higher than the values for self-diffusion of the constituent cations, being in the range of 4.5–5 eV.² It was concluded² that in YSZ, the diffusion occurs via free cation vacancies $V_{\text{Zr}}^{4'}$ formed by a Schottky reaction in ZrO_2 ,³ while in CSZ, the self-diffusion goes via vacancies associated to oxygen

TABLE I. Summary of the experimental results for lanthanides diffusion in YSZ and CSZ and comparison with literature data on self-diffusion in these materials (lower part of table).

Ion	Ionic radius (Å)	Activation enthalpy (eV)		$\ln[D_0/\text{cm}^2/\text{s}]$	
		YSZ	CSZ	YSZ	CSZ
Sc ³⁺	0.87	5.0±0.2	4.1±0.9	0.6±1.4	-4±6
Lu ³⁺	0.97	4.9±0.2	6.2±0.5	0.2±0.2	9±3
Yb ³⁺	0.98	4.9±0.3	6.0±0.6	0.01±1.7	8±4
Tm ³⁺	0.99	5.1±0.1	6.1±0.8	1.2±0.8	8±5
Y ³⁺	1.015		5.8±0.7		7±4
Ho ³⁺	1.02	5.4±0.1	5.6±1.2	2.5±0.6	5±8
Dy ³⁺	1.03	5.2±0.1	5.9±0.8	2.2±0.9	8±6
Tb ³⁺	1.04	5.2±0.2	5.8±1.2	1.9±1.5	7±8
Gd ³⁺	1.06	5.4±0.2	6.4±0.8	4.1±1.6	12±5
Eu ³⁺	1.07	5.2±0.2	5.9±1.5	2.2±1.5	8±11
Sm ³⁺	1.09	5.2±0.2	6.3±0.8	2.2±1.6	12±5
Nd ³⁺	1.12	4.7±0.3	6.1±0.7	-0.4±1.8	10±5
Pr ³⁺	1.14	5.3±0.2	5.7±0.7	3.6±1.4	8±7
Ce ³⁺	1.14	5.1±0.3	6.6±0.9	2.4±2.0	14±6
La ³⁺	1.18	5.0±0.4	5.6±0.6	1.3±2.7	7±4
Zr ⁴⁺	0.84	4.7±0.2 ^a	5.1±0.3 ^b	-2.3 ^a	1.7 ^b
Y ³⁺	1.02	4.2±0.8 ^d	5.2±0.5 ^a	-3.7 ^d	3.5 ^a
Ca ²⁺	1.12	3.5±0.3 ^c	5.6±0.1 ^b	-5.6 ^c	7.4 ^b

^aReference 3.^bReference 2.^cReference 5.^dReference 14.

vacancies.² These cation vacancies should not be bound to oxygen vacancies despite their high charge. We assume that this mechanism should also govern the diffusion of the lanthanides in CSZ and YSZ, both because of their similar activation enthalpy and also because of the chemical similarities. When comparing the values of the diffusion coefficient for a lanthanide in CSZ and YSZ (see Fig. 4 for the example of samarium), one can see that the lanthanide diffusion in YSZ is slower than in CSZ.

The connection between experimental and simulation results can be done by comparing the activation enthalpies. The experimental values for lanthanide diffusion in CSZ are around 6.0 eV (578 kJ/mol) and include at least both the formation enthalpy and the migration enthalpy, without a significant dependence 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 dependence on the lanthanide ionic radius, while the Jackson values range from 3.5 to 5.2 eV, but are also centered around 4.5 eV. While the Jackson potential set was developed for lanthanide halides, the Grimes potential set is developed for lanthanide doped ceria and pyrochlores, which are much more similar to the investigated system than the lanthanum halides used for developing the Jackson potentials. Generally, halides have higher ionic radii than oxides and they are “softer,” i.e., their polarizability is higher than in “hard” oxides. These effects lead to the observed behavior of the migration energies, in particular, to the much stronger variation (1.5 eV in contrast to 0.3 eV) of the migration energy, and the role of ionic polarization is less influential on cation diffusion in zirconia. Therefore, the comparison of the experimental and calculated activation energies will be focused on the results obtained with the Grimes potential sets. 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 proceeds via complex defects $[V_{\text{Zr}}^{4'}, 2V_{\text{O}}^{2*}]^x$ and the experimental activation enthalpy should be a sum of the migration enthalpy, a formation and an association term.² The calculated values represent the migration enthalpy, and therefore, the difference of 1.5 eV can be attributed to the sum of the formation enthalpy of the isolated defects, i.e., $V_{\text{Zr}}^{4'}$ and the $2V_{\text{O}}^{2*}$, and their association enthalpy to form the defect $[V_{\text{Zr}}^{4'}, 2V_{\text{O}}^{2*}]^x$. Since the formation energy cannot be negative, one can share the association enthalpy equally between the association of the first and the second oxygen vacancy. In doing so, one gets a value of 0.75 eV for the upper limit of the association enthalpy of a cation vacancy with one oxygen vacancy. A significant value for the formation energy should reduce this value more.

In YSZ, the activation enthalpies for lanthanide diffusion were smaller by 1 eV than the values observed for CSZ.¹ Similarly, the self-diffusion activation enthalpies of the host cations were between 4 and 5 eV,³ also up to 1 eV smaller than found for the host cations in CSZ.² It was concluded that in YSZ the cation diffusion proceeds 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 diffusion coefficients and calculated migration enthalpies, a change in the ionic radius dependency of the evaluated parameters around 1.0 Å was observed in both cases although it is not very pronounced for the migration enthalpies calculated with the

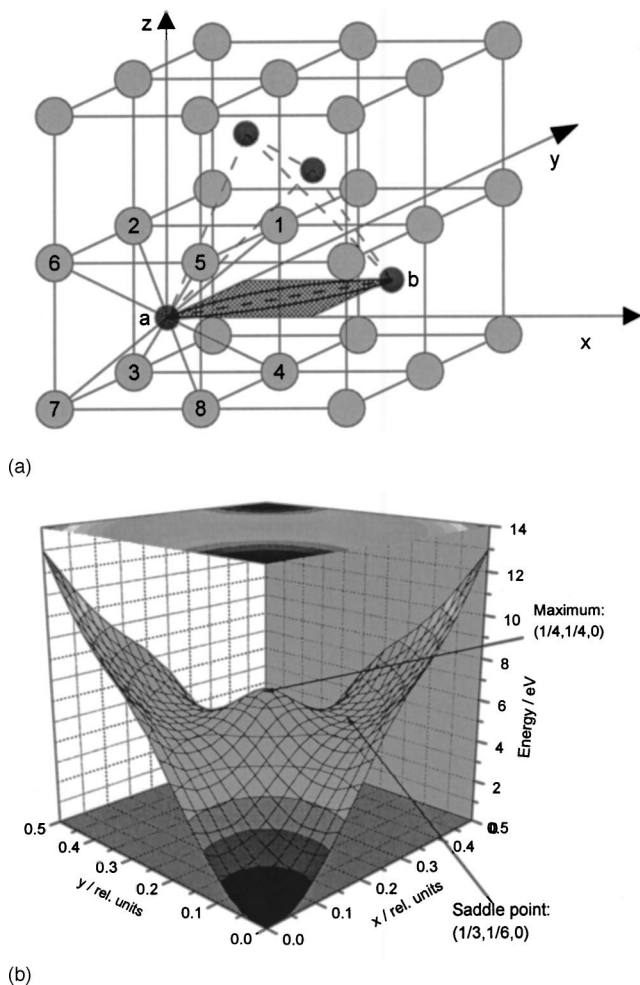


FIG. 5. Energy map for Zr^{4+} migration in perfect cubic zirconia. (a) Schematic drawing of the fluorite lattice. Two cation vacancies are placed at $(0,0,0)$ and $(1/2,1/2,0)$, and one Zr^{4+} ion is intermittently moved between the two positions in the whole gray plane at $z=0$. (b) Resulting energy map, showing the saddle point energy of 7 eV and the migration energy of 5 eV.

Grimes potential: below this value, the diffusion coefficient is constant and then increases by a factor of 3–5. Given a constant preexponential factor one needs to decrease the activation enthalpy by about 0.22 eV in order to increase the

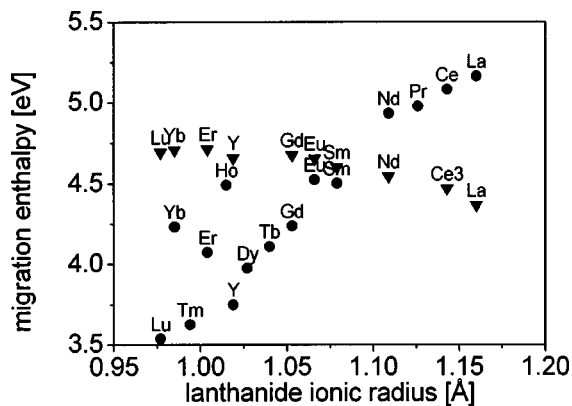


FIG. 6. Computer simulation of cation migration enthalpies in cubic zirconia using parameter sets of Jackson (circles) (Ref. 11) and Grimes (triangles) (Ref. 12).

diffusion coefficient by a factor of 5. Since the experimental error in determining the activation enthalpy is of this order (see Table I), it is difficult to observe such a small effect in the activation enthalpies conclusively. Therefore, a migrating cation in cubic zirconia seems not to be affected by its local surroundings 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.

These results correspond also to calculations of the Flory-Huggins χ thermodynamic interaction parameters in fluorite-type solid solutions of zirconia with lanthanides and some transition metals made by Yokokawa (Ref. 15) (Fig. 4 in Ref. 15; this figure is ambiguously labeled). He observed for the lattice stability of threefold-charged cations (Ln^{3+} and others) that it has a minimum value between 0.9 and 1.1 Å, while it is decreasing with increasing ionic radius for Me^{2+} transition metals. It is interesting to note that this behavior is reflected in the cation diffusion in zirconias: Qualitatively, the diffusion coefficients increase as the interaction enthalpy calculated by Yokokawa become higher. The difference in interaction enthalpy within the lanthanides is according to Yokokawa about 15 kJ/mol. This corresponds to a change in the activation enthalpy of 0.17 eV, less than the changes in the migration enthalpy calculated either using the Grimes potential set (0.5 eV) and the Jackson potential set (nearly 2 eV). Alternatively, the variation of the interaction enthalpy corresponds to a variation in the diffusion coefficient by a factor of 3, if one assumes a constant preexponential factor. This is close to the variation of the experimentally observed diffusion coefficients (Fig. 2).

According to the theoretical calculations of Yokokawa, the interaction parameter should start being a function of the ionic radius above an ion radius of 1.1 Å. For the lanthanide diffusion experiments made here, the diffusion coefficients start to become dependent on the ionic radius above 1.0 Å. Regarding the diffusion of Sc^{3+} being only slightly faster than the diffusion of Zr^{4+} , we found significantly lower values than for both the lanthanides and the host self-diffusion. That could mean that scandium diffusion in CSZ seems to be governed by another type of transport process, probably by the migration via nonassociated defects.

With a value of $(1.2-6)k_B$, the entropies of diffusion in YSZ also support a diffusion mechanism going via free vacancies.¹⁶ According to Solier *et al.*, for simple vacancy diffusion processes, an entropy of $3k_B$ for migration and $3k_B$ for formation of the vacancies are typical values for the two processes. The values for YSZ are in general slightly lower, but since the determination of the activation entropy is more erroneous than the determination of the activation enthalpy, they still support the diffusion via free vacancies. In contrast, the entropies of migration in CSZ are significantly higher, between $10k_B$ and $20k_B$. These large values are due to the fact that the lanthanide diffusion goes via vacancy complexes of the type $[V_{Zr}^{4+}, 2V_O^{2-}]^x$. Since three vacancies need to move here, the activation entropy should contain three times the contribution of $3k_B$ for migration, and one may even expect a value of $12k_B$ for the total activation entropy of diffusion.

Kowalski *et al.*^{5,6} found that the bulk diffusion coeffi-

cations in YSZ for the larger ion Ca^{2+} are higher than for the smaller Ti^{4+} , similar to the findings in earlier self-diffusion study.² The lanthanides investigated are considered threefold charged. They show the same behavior as observed by Kowalski, namely, the smaller cations have a lower diffusion coefficient than larger ions. 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 get a better insight into this problem.

V. CONCLUSIONS

The diffusion of lanthanides was studied experimentally in single crystalline CSZ and YSZ between 1286 and 1460 °C (CSZ) and 1250 and 1600 °C (YSZ). Lanthanide migration enthalpies were calculated using the Mott-Littleton approach. The following key results were obtained.

(1) The bulk diffusion coefficient depends on the ionic radius of the lanthanide tracer. For radii smaller than 1 Å, it is constant and roughly identical to the zirconium self-diffusion coefficient, while for larger ionic radii, the diffusion coefficient approaches the stabilizer diffusivity. This effect is similarly found for the lanthanide diffusion in YSZ and in CSZ indicating that the cation transport is limited by the size of the host cation and not by the size of the stabilizer.

(2) The experimental activation enthalpies are about 6 eV for CSZ and between 4 and 5 eV for YSZ and almost constant for all lanthanides. The Mott-Littleton calculations yield migration enthalpies decreasing slightly from 4.7 to 4.4 eV with increasing ionic radius. This means that the sum of the formation enthalpies and the association enthalpies

would be as low as 1.5 eV for CSZ, and nearly 0 eV for YSZ, which is in contrast to theoretical calculations of formation enthalpies in CSZ yielding values below 1 eV.

(3) The cation diffusion coefficients can be correlated to the interaction energies between ZrO_2 and the lanthanide oxide: The higher the interaction energy, the higher the cation diffusion coefficient.

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