Grain Boundary Mobility in Y$_2$O$_3$: Defect Mechanism and Dopant Effects

Pei-Lin Chen* and I-Wei Chen*

Department of Materials Sciences and Engineering, University of Michigan, Ann Arbor, Michigan 48109-2136

The effects of the dopants, Mg$^{2+}$, Sr$^{2+}$, Se$^{4+}$, Yb$^{3+}$, Gd$^{3+}$, La$^{3+}$, Ti$^{4+}$, Zr$^{4+}$, Ce$^{4+}$, and Nb$^{5+}$, on the grain boundary mobility of dense Y$_2$O$_3$ have been investigated from 1500° to 1650°C. Parabolic grain growth has been observed in all cases over a grain size from 0.31 to 12.5 μm. Together with atmospheric effects, the results suggest that interstitial transport is the rate-limiting step for diffusive processes in Y$_2$O$_3$, which is also the case in CeO$_2$. The effect of solute drag cannot be ascertained but the anomalous effect of undersized dopants (Ti and Nb) on diffusion enhancement, previously reported in CeO$_2$, is again confirmed. Indications of very large binding energies between aloivalent dopants and oxygen defects are also observed. Overall, the most effective grain growth inhibitor is Zr$^{4+}$, while the most potent grain growth promoter is Sr$^{2+}$, both at 1.0% concentration.

I. Introduction

Our recent experimental studies of grain boundary mobility in CeO$_2$, a fluorite-structured oxide, have revealed several important features. First, grain boundary mobility is controlled by cation diffusivity, and cations diffuse by an interstitial mechanism that can be enhanced by the presence of oxygen vacancies. Second, at high dopant concentrations, a solute drag mechanism operates that can suppress grain boundary mobility. Third, grain boundary mobility is influenced by dopant-defect interaction which is charge and size dependent. Fourth, severely undersized dopants have a tendency to markedly enhance grain boundary mobility, probably due to the distortion of the surrounding lattice that apparently facilitates defect migration. These new results are consistent with other reports on the structure, energetics, and kinetics of the CeO$_2$ system. In fact, a review of the previous data in the literature suggests that the cation interstitial mechanism may be general for hypostoichiometric fluorite-structured oxides (AO$_{2-n}$). For example, self-diffusivity of U has been reported to increase with x at x > 0.02 in UO$_{2-x}$, Likewise, creep and evaporation studies in U$_{1-x}$P$_2$O$_{7-x}$ and grain growth studies in U$_{1-x}$Ca$_x$O$_{2-x}$ both witnessed enhanced kinetics with increasing x. These observations are consistent with a cation interstitial mechanism which may be justified by the availability of large, unoccupied interstitial sites in the fluorite structure.

Y$_2$O$_3$ has a C-type rare-earth oxide crystal structure. As shown in Fig. 1, this structure may be pictured as a modified fluorite-type cubic structure with one fourth of the anion sites vacant and regularly arranged. Like fluorite-structured oxides, oxygen vacancies and interstitials are the major defects in pure yttrium oxide. Also like fluorite-structured oxides, Y$_2$O$_3$ can dissolve a large amount of aloivalent cations. This is accompanied by creating charge-compensating oxygen vacancies when acceptor dopants are present, and oxygen interstitials when donor dopants are present. These anion defects facilitate oxygen diffusion. Indeed, it is known that oxygen anion diffusion is much faster than yttrium cation diffusion in pure Y$_2$O$_3$. Thus, cation diffusion is the rate-controlling step for grain boundary migration at all compositions. Since cation doping can be readily conducted within the solubility limit, Y$_2$O$_3$, like CeO$_2$, is a good candidate for investigating cation dopant effects on grain boundary mobility. The cubic symmetry of this oxide further assures a lack of strong anisotropy in grain boundary mobility which could otherwise complicate grain growth behavior.

In order to understand the effects of dopants on mobility, oversized and undersized dopants of both donor and acceptor types are investigated. They include, in the order of increasing charge and size, Mg$^{2+}$, Sr$^{2+}$, Se$^{4+}$, Yb$^{3+}$, Gd$^{3+}$, La$^{3+}$, Ti$^{4+}$, Zr$^{4+}$, Ce$^{4+}$, and Nb$^{5+}$, all of which have also been investigated in our grain growth study of CeO$_2$. Since Y$^{3+}$ and Ce$^{4+}$ have very similar ionic radii for both 6-fold (as in C-type structure) and 8-fold (as in fluorite structure) coordination, a direct comparison of the dopant behavior in these two closely related oxide structures is possible. Table I summarizes the literature data of ionic radius, solubility, and Vegard’s slope (on the basis of cation percent) of these dopants.

II. Theoretical Considerations

Following the analysis of defect chemistry for CeO$_2$ in our previous paper, we estimate the defect concentration in Y$_2$O$_3$ in the following way. Starting with

![Diagram](image)

Fig. 1. Crystal structure of Y$_2$O$_3$. Three quarters of cations are in cubes in which the missing oxygens are along a face diagonal. One quarter of cations are in cubes in which the missing oxygens are along a body diagonal.

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Table I. Ionic Radius, Vegard’s Slope, and Solubility of MO₃ in Y₂O₃

<table>
<thead>
<tr>
<th>Ion</th>
<th>Ionic radius (Å)</th>
<th>Vegard’s slope</th>
<th>Solubility (%MO₃)</th>
<th>References</th>
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<tr>
<td>Mg²⁺</td>
<td>0.72</td>
<td>0.0989</td>
<td>1 (1700°C)</td>
<td>18</td>
</tr>
<tr>
<td>Sr⁰⁺</td>
<td>1.18</td>
<td>1</td>
<td>1 (1700°C)</td>
<td>12, 19</td>
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<tr>
<td>Sc³⁺</td>
<td>0.745</td>
<td>0.868</td>
<td>100</td>
<td>20</td>
</tr>
<tr>
<td>Yb³⁺</td>
<td>0.9</td>
<td>0.9</td>
<td>70 (1600°C)</td>
<td>21</td>
</tr>
<tr>
<td>Y³⁺</td>
<td>1.032</td>
<td>0.605</td>
<td>10 (1400°C)</td>
<td>22</td>
</tr>
<tr>
<td>Gd⁴⁺</td>
<td>0.938</td>
<td>0.72</td>
<td>25 (1600°C)</td>
<td>23</td>
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<tr>
<td>La³⁺</td>
<td>0.87</td>
<td>0.87</td>
<td>28 (1600°C)</td>
<td>14</td>
</tr>
<tr>
<td>Tb⁴⁺</td>
<td>0.64</td>
<td>0.64</td>
<td>30 (1500°C)</td>
<td>24</td>
</tr>
</tbody>
</table>

1Reference 17. All for 6-fold coordination. 2ΔV/V₀ = αC (α = Vegard’s slope, C = solute atomic fraction, V₀ = unit-cell volume of pure Y₂O₃).

Schottky defect for cation:

\[ \text{null} \xleftrightarrow{\Delta G^{\text{c}}_\text{c}} 2V^{m+}_\text{c} + 3V^{0+}_\text{c} \]  
(1)

Frenkel defect for cation:

\[ Y^{m+}_\text{c} \xleftrightarrow{\Delta G^{\text{c}}_\text{c}} Y^{m+}_\text{c} + V^{0+}_\text{c} \]  
(2)

Frenkel defect for anion:

\[ O^{m-}_\text{o} \xleftrightarrow{\Delta G^{\text{o}}_\text{o}} O^{m-}_\text{o} + V^{0+}_\text{c} \]  
(3)

we obtain

\[ [V^{m+}_\text{c}] = [V^{0+}_\text{c}]^{-1.5} K^{0.5}_\text{c} \exp \left( \frac{-\Delta G^{c}/2}{kT} \right) \]  
(4)

\[ = [O^{m-}_\text{o}]^{-1.5} K^{0.5}_\text{c} \exp \left( \frac{-\Delta G^{0}/2 - 3\Delta G^{c}/2}{kT} \right) \]  
(5)

\[ [Y^{m-}_\text{c}] = [V^{0+}_\text{c}]^{-1.5} K^{0.5}_\text{c} \exp \left( \frac{-\Delta G^{c} - \Delta G^{0}/2}{kT} \right) \]  
(6)

\[ = [O^{m-}_\text{o}]^{-1.5} K^{0.5}_\text{c} K^{1.5}_\text{c} \exp \left( \frac{-\Delta G^{c} - \Delta G^{0}/2 + 3\Delta G^{0}/2}{kT} \right) \]  
(7)

In the above, \( K^{0}_\text{c} \), \( K^{0}_\text{c} \), and \( K^{0}_\text{c} \) are the preexponential, temperature-independent, factors of the reaction constants of (1), (2), and (3), respectively. Cation diffusivity, which is proportional to the cation defect concentration, is thus strongly dependent on the concentration of oxygen defects.

In pure Y₂O₃, oxygen defect concentrations are determined by the following reactions:

Oxidation (p-type):

\[ \frac{1}{2}\text{O}_2 \xleftrightarrow{\Delta G^{0}_\text{o}} O^{0+}_\text{o} + 2h^+ \]  
(8)

Reduction (n-type):

\[ O^{0-}_\text{o} \xleftrightarrow{\Delta G^{0}_\text{o}} V^{0+}_\text{o} + 2e^- + \frac{1}{2}\text{O}_2 \]  
(9)

Along with the reaction of anion Frenkel defects (Eq. (3)), we obtain

p-type:

\[ [V^{0+}_\text{c}] = K^{0}_\text{c} K^{0.5}_\text{c} \exp \left( \frac{-\Delta G^{0}_\text{o} - 3\Delta H^{0}_\text{o}/3}{kT} \right) \propto P^{0.5}_\text{o} \]  
(10)

n-type:

\[ [O^{m-}_\text{o}] = K^{0}_\text{c} K^{0.5}_\text{c} \exp \left( \frac{-\Delta H^{0}_\text{o}/3}{kT} \right) \propto P^{0.5}_\text{o} \]  
(11)

In the above, \( K^{0}_\text{c} \) and \( K^{0}_\text{c} \) are the preexponential, temperature-independent but pressure-dependent, factors of reaction constants of (8) and (9), respectively. According to Tallen and Vest, \( Y_2O_3 \) exhibits p-type conduction at low temperature and high oxygen pressure, and n-type conduction at high temperature and low oxygen pressure. This n–p boundary is shown in Fig. 2(a) to guide our analysis. Our experiments on undoped \( Y_2O_3 \) were conducted mostly at room temperature, we therefore expect p-type behavior. This information on conductivity allows us to approximately estimate the concentration of intrinsic defects, \( [O^{m-}_\text{o}] \) in the case of p-type and \( [V^{0+}_\text{c}] \) in the case of n-type, by assuming a reasonable value for the mobility of electrons and holes (\( \mu_e = \mu_h = 10^{-3} \text{ cm}^2/\text{V} \cdot \text{s} \)). The calculated results are shown in Fig. 2(b) as a function of oxygen partial pressures. It is clear from Fig. 2(b) that under our experimental conditions, the concentration of intrinsic defects is very low indeed and it would be rather unrealistic to attempt to control the dopant concentration to comparably low values. Therefore, unlike in our CeO₂ study, we have not studied the dopant effect in the intrinsic regime but instead limited ourselves to the extrinsic regime in large part.

In the extrinsic regime, every two divalent acceptors create one \( V^{0+}_\text{c} \). This increases \( [Y^{m-}_\text{c}] \) but decreases \( [V^{0+}_\text{c}] \). Conversely, every two tetravalent donors create one \( O^{0-}_\text{o} \), so that \( [V^{0+}_\text{c}] \) is increased but \( [Y^{m-}_\text{c}] \) is decreased. Since grain boundary mobility is directly proportional to cation diffusivity regardless of whether it is grain boundary or lattice diffusion (solute drag) controlled, grain growth studies under different atmospheres together with different dopants in the extrinsic regime allow us to indirectly determine the diffusion mechanism in \( Y_2O_3 \). These findings can then be compared with those in CeO₂.

### III. Experimental Procedure

Monosized spherical yttria powders were first prepared following a homogeneous precipitation method which was similar to the one used by Sorodelet and Akinc. Ì™¬ Yttrium nitrate (Y(NO₃)₃, Alfa) and urea (NH₄H₂O, Fisher) were used as starting materials. After being calcined at 700°C in air for 1.5 h, the obtained yttria powders, with a particle size of 0.23 μm, were dispersed in isopropyl alcohol to which a desired amount of dissolved dopant nitrate was added. (Dopant concentrations were fixed at 1.0% of the total cations. This is the same amount used in the CeO₂ study in the extrinsic regime.) The slurry was poured through a 20 μm nylon screen and dried under heat while being stirred. The dried powders were sintered through a
100 μm nylon screen and recalcined. Throughout the above process, plastic ware was used to avoid silica contamination.

The calcined powders were dry-pressed into pellets with a diameter of 10 mm and further isostatically pressed at 310 MPa. The green density after isostatic pressing was about 43% of the theoretical density. For sintering, a constant heating rate, 10°C/min, was chosen to reach the desired temperatures ranging from 1500°C to 1650°C. Samples were held there from 1 to 63 h, and furnace cooled. To minimize silica contamination, firing in air was conducted using a dedicated "clean" furnace. Flowing gas of 2% H₂ in Ar was also used in a tube furnace when a reducing atmosphere was needed.

The microstructures of the sintered specimens were characterized by scanning electron microscopy (SEM) after polishing and thermal etching. The grain size was obtained for samples with a density higher than 99% by multiplying the average linear intercept length of at least 500 grains by 1.56.⁴

IV. Results

(1) Microstructure

Figure 3 shows selected microstructures to demonstrate the difference in grain size. Among all the dopants, Zr-doped Y₂O₃ has the smallest grain size, while Sr-doped Y₂O₃ has the largest one, under the same sintering conditions. As shown in Figs. 3(b) and (d), the grain size of Sr-doped Y₂O₃ is more than 10 times that of Zr-doped Y₂O₃. Abnormal grain growth seems absent in these microstructures. To ascertain this, grain size distributions were measured and plotted in a normalized form in Fig. 4. They appear to follow each other closely, centering around the mean grain size, despite the large difference in the average grain size. Thus, a time-invariant grain size distribution has been attained in our experiments. It also justifies our use of the mean grain size to characterize grain growth kinetics.

(2) Grain Boundary Mobility

Following the procedure established in our previous papers,¹² we found that the mobility data agree with the parabolic law well:

\[ d^2 - d_o^2 = 2M_γ(t - t_o) \]  \hspace{1cm} (14)

In the above \( d_o \) is the reference grain size at time \( t_o \), \( d \) is the average grain size at time \( t \), and \( γ \) is the grain boundary energy. To avoid the effect of porosity on grain growth, \( t_o \) was appropriately chosen so that porosity was less than 1%. Typically, it lies between 3 h at 1500°C and 1 h at 1650°C. If the mobility and grain boundary energy are not a function of time (or grain size), then Eq. (14) predicts a straight line relation between \( d^2 - d_o^2 \) and \( t - t_o \). This relation is demonstrated in Fig. 5, from which the slope can be computed to obtain \( 2M_γ \). Since the value of the slope varies over several orders of magnitude, it most likely reflects the large influence of the dopants on grain boundary mobilities. (Grain boundary energy typically varies by no more than a factor of 2 or 3 only.) In view of this, we have used \( γ = 0.3 \) J/m² in our previous work to obtain an estimate of the mobility. The same practice is also adopted here. The mobilities evaluated in this way are tabulated in Table II for future reference. These data are analyzed in the following to elucidate the diffusion and grain growth mechanisms.

V. Cation Interstitial Mechanism

(1) Undoped Y₂O₃

The grain boundary mobility of pure Y₂O₃ is higher in reduced atmosphere than in air. These data are shown in Fig. 6 and clearly indicate cation diffusion is via the cation interstitial mechanism. In the intrinsic regime, the temperature dependence of [\( Y_z^{+} \)]_t can be analyzed by combining Eqs. (7) and (11) for the p-type or Eqs. (6) and (12) for the n-type.

p-type:

\[ [Y_z^{+}]_t = \frac{K_p K_F^{A1S}}{K_S^{O2S}} \times \exp \left[ \frac{-\Delta G_e - \frac{\Delta G_o}{2} + \frac{3\Delta G_b}{2} - \frac{\Delta H_{OZ}^{(0)}}{2}}{kT} \right] \]  \hspace{1cm} (15)

n-type:

\[ [Y_z^{+}]_t = \frac{K_p K_F^{P2S}}{K_S^{O2S}} \times \exp \left[ \frac{-\Delta G_e - \frac{\Delta G_o}{2} + \Delta H_{OZ}^{(0)}}{kT} \right] \]  \hspace{1cm} (16)

From the conductivity data of Tallen and Vest,²⁵ we estimate \( \Delta H_{OZ}^{(0)} = 5.82 \) eV, and \( \Delta H_{OZ}^{(0)} = 11.2 \) eV. Furthermore, Odier
Fig. 3. Microstructures of undoped and doped Y$_2$O$_3$ sintered at 1500°C for 27 h: (a) Y$_2$O$_3$, (b) 1.0% Sr, (c) 1.0% Yb, (d) 1.0% Zr, (e) 1.0% Nb.

... and Lupo reported that the thermal band gap is about 5.5 eV. These data allow us to obtain from Eqs. (3), (8), and (9), $\Delta G^\circ = 6.0$ eV. From consideration of the defect reaction

$$3V^\cdot + 2Y^\cdot \xrightarrow{\Delta G^\circ} 2Y_2^\cdot \tag{17}$$

we believe the energy $\Delta G^\circ - \Delta G_s/2$ should be nonnegative since anion defects should be easier to move than cation defects in Y$_2$O$_3$. This then places an upper bound of the activation energy of [Y$^\cdot_2$] at 6.1 eV in p-type and 5.6 eV in n-type. These values are higher than the measured activation energy of grain boundary mobility, 4.1 eV for p-type (in air) and 3.7 eV for n-type (in 2% H$_2$). The reason for the overestimation probably lies in the overestimate of $\Delta G^\circ$ in the previous work. For UO$_2$, a nonstoichiometric compound, this value is much lower, 3.0 eV.\cite{29} Values around 6.0 eV are more typically associated with highly stoichiometric compounds such as BeO and MgO.\cite{30} For Y$_2$O$_3$, which is more like a nonstoichiometric compound such as UO$_2$ than BeO or MgO, it seems that an estimate of $\Delta G^\circ$ around 4.5 eV is more reasonable. This gives an activation energy of 3.8 eV for the p-type. If we use the same $\Delta G^\circ$ to revise the estimate of $\Delta H^\circ$ to be 9.7 eV, we also arrive at an activation energy of 4.8 eV for the n-type. These estimates compare more reasonably with our data on grain boundary...

Fig. 4. Grain size distributions of undoped and doped Y$_2$O$_3$. Grain size is normalized by mean grain size in each case, which varies from 0.73 to 9.7 μm.

Fig. 5. Grain growth kinetics of Y$_2$O$_3$ at 1500°C; dopants as indicated.
mobility provided the activation energy for interstitial migration is nearly zero. (The same observation on migration energy was previously made for cation migration in the grain boundary in CeO₂.)

(2) Acceptor and Donor Doping

We now consider divalent and tetravalent dopants. We first compare the mobility data of undoped Y₂O₃ and those doped with Sr⁺ and Zr⁴⁺. These data are shown as solid lines in Fig. 7. We have also included dopants which either are much smaller (Mg⁹⁺ and Nb⁵⁺) or have a tendency to reduce to lower valence states (Ti⁺ and Ce⁺⁺) and plot their data as dashed lines in Fig. 7. The solid lines in Fig. 7 show a clear trend of acceptor dopant enhancing grain boundary mobility, whereas donor dopants do the opposite. This trend is consistent with the cation interstitial mechanism.

The activation energy for acceptor doping is typically higher than that for undoped Y₂O₃, which is in turn higher than that for donor doping. (Ti doping is an exception; in this case, charge consideration is complicated by mixed valence states.) This has the consequence of making the enhancement/suppression effects of dopants more pronounced at higher temperatures than at lower temperatures. In the context of the interstitial mechanism, this implies a higher relative concentration of [V₉⁺] (for acceptor doping) or [O⁷⁻] (for donor doping), compared with undoped Y₂O₃, as the temperature increases. A simple interpretation of this observation is that the extrinsic defects are bound to the dopants at lower temperatures, and become dissociated only at higher temperature, rendering the dopant effect on [Y⁻⁻] increasingly obvious. As schematically shown in Fig. 8, this can cause the mobility in the intermediate temperature range to take a different activation energy in a way that is consistent with our observations.

Because of the lack of reliable data for various energies in Y₂O₃, an accurate estimate of the association energy between defects and dopants cannot be obtained at this time. For a rough estimate, though, we let ΔG₉⁻ - ΔG₉⁻/2 = 0 (say ΔG₉ = 5 eV and ΔG₅ = 10 eV). Then, for acceptor doping, we expect Eq. (6) to apply. The contribution to the activation energy, except that for V₉ and for interstitial migration, is ΔG₉ - ΔG₉/2, which is zero. Thus, the very large activation energy of grain boundary mobility (5.3 eV for Sr doping) is mostly due to a very strong binding between V₉ and acceptor dopants, of the order of 3.6 eV (Y⁻⁻ ≈ [V₉⁺]⁻⁻). For donor doping, we expect Eq. (7) to hold. The contribution to the activation energy, except that for O⁷⁻ and for interstitial migration, is ΔG₉ - ΔG₉/2 + 3ΔG₅/2, or 6.7 eV if ΔG₉ - ΔG₅/2 is zero. Thus, the very small activation energy for grain boundary mobility (0.7 eV for Zr doping) is mostly due to a very strong binding energy between O⁷⁻ and donor dopants, of the order of 4 eV (Y⁻⁻ ≈ [O⁷⁻]⁻⁻).

Other data of acceptor and donor doping can be rationalized by taking into account additional effects associated with dopant size and charges. Mg⁹⁺ doping is less effective than Sr⁷⁺ doping in enhancing mobility and it has a higher activation energy. This may be attributed to an even stronger binding between V₉ and Mg, presumably due to the larger elastic distortion associated with the undersized dopant as discussed in our CeO₂ paper. Ce⁶⁺ doping has a smaller suppression effect on mobility than Zr⁴⁺ doping, presumably because Ce⁺⁺ tends to reduce to Ce¹⁺ at higher temperature, thus decreasing the net effect of...
donor doping, and decreasing the activation energy somewhat.

Table II  Grain Boundary Mobility of Undoped and 1.0%-Doped Y$_2$O$_3$ in Air

<table>
<thead>
<tr>
<th></th>
<th>1500°C</th>
<th>1550°C</th>
<th>1600°C</th>
<th>1650°C</th>
<th>Activation energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y$_2$O$_3$</td>
<td>1.7</td>
<td>3.5</td>
<td>7.9</td>
<td>13.6</td>
<td>4.14</td>
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<tr>
<td>Mg$^{4+}$</td>
<td>6.4</td>
<td>20</td>
<td>70</td>
<td>159</td>
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<tr>
<td>Sr$^{2+}$</td>
<td>53</td>
<td>251</td>
<td>584</td>
<td>965</td>
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<td>0.86</td>
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<td>2.4</td>
<td>2.82</td>
</tr>
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</table>

VI. Discussion

1) Grain Boundary Mobility

Kinetic studies on the dopant effects on Y$_2$O$_3$ have been reported by various authors.

2) Trivalent Dopants

Doping by trivalent dopants, in principle, should not affect defect population and thus has no effect on grain boundary mobility. Trivalent dopants, however, generally increase the grain boundary mobility somewhat, by a factor of 2–5 times, but the enhancement effect is much smaller than that caused by acceptor dopants. This is shown in Fig. 9, which includes all the trivalent dopant data along with those of undoped Y$_2$O$_3$. Since the activation energy of these doped Y$_2$O$_3$ is generally comparable to that of undoped Y$_2$O$_3$, around 4 eV, it suggests the same grain boundary diffusion mechanism. The modestly enhanced mobility may be due to a slight distortion of the lattice or a slight modulation of the phonon vibration spectra that leads to a slightly higher migration rate for the cation interstitial and hence a modestly higher mobility. Alternatively, it may also be due to the disordering effect of solid solution that could perturb the ordering of unoccupied anion sites in Fig. 1, although the exact cause of these dopant effects cannot be ascertained at this time.

Fig. 9. Effect of 1.0% trivalent dopants on the grain boundary mobility in Y$_2$O$_3$. 

10000/T (K$^{-1}$)

[Graph showing mobility vs. temperature for various dopants like Gd, La, Sc, Y$_2$O$_3$, Yb]
to study diffusion-enhancing solutes in materials that have $\mathcal{D}_B >> \mathcal{D}_L$.

Selected data of grain boundary mobility of $Y_2O_3$ and CeO$_2$ systems are plotted in Fig. 11 to outline the broad range of mobility values in these materials. It is clear that $Y_2O_3$ has generally lower mobility than CeO$_2$ at the same temperature. This is not due to a different homologous temperature, since $Y_2O_3$ actually has a slightly lower melting point (2410°C) than CeO$_2$ (2600°C). Indeed, comparing $Y_2O_3$ with other fluorite-structure oxides, such as tetragonal ZrO$_2$ and cubic ZrO$_2$, also shown in Fig. 11, we find Y$_2$O$_3$ has a much lower grain boundary mobility than these oxides. (The melting point of ZrO$_2$ is 2700°C.) This may indicate that the grain boundary diffusivities of doped and undoped Y$_2$O$_3$ are relatively low and are already close in magnitude to those of lattice diffusivity. Thus, according to Fig. 10, this would cause some difficulty in demonstrating the solute drag effect. Although further studies of the concentration effect may prove insightful, they are unfortunately limited by the relatively low solubility of both of the diffusion-enhancing dopants, Mg and Sr, investigated here (see Table I).

(2) Defect Chemistry

A further comparison of the defect chemistry in Y$_2$O$_3$ and fluorite-structure MO$_2$ can be made on the much larger interaction energy between divalent dopant and anion defects in Y$_2$O$_3$ and on the difference in Nb solubility. Regarding the former, we note that according to our study, a binding energy of the order of 3–4 eV exists between divalent dopants and anion defects. This contrasts with a much smaller, by 1 order of magnitude, binding energy in CeO$_2$, which has been consistently inferred by the data of ionic conductivity$^{29,30}$ and grain boundary mobility.$^3$ A crude estimate of the Coulombic binding energy can be made in the form (in cgs units) of $4\varepsilon^2/\varepsilon r$, where $\varepsilon$ is elementary charge, $\varepsilon$ is the dielectric constant, and $r$ is the nearest distance between cation dopant and anion defects. In the above, the factor 4 in the numerator arises from the effective charge of anion defects and the fact that two divalent cations (Sr$^{2+}$ or Zr$^{4+}$, for example) are likely to cluster around one anion defect. Using $\varepsilon = 4.64$ and $r = 2.2$ Å (for V$_0$) to 2.5 Å (for O)$^{39,40}$ an estimate from 4.95 to 5.63 eV is obtained. In CeO$_2$, such Coulombic energy contribution is largely lowered due to elastic and dielectric relaxation of the matrix.$^{41}$ In Y$_2$O$_3$, however, recent preliminary lattice static calculation using the Mott–Littleton model seems to at least partially validate the large magnitude of the above estimate.$^{42}$ This suggests a much more ionic matrix in Y$_2$O$_3$ which does not relax to the same extent as in CeO$_2$.

We note that in both CeO$_2$ and ZrO$_2$, the solubility of Nb$^{5+}$ is very limited, indicating difficulty in generating O$_0$. This is in contrast with the large Nb$^{5+}$ solubility in Y$_2$O$_3$ (see Table I). Thus, it seems that both V$_0$ and O$_0$ are equally likely to form in Y$_2$O$_3$, whereas CeO$_2$ and ZrO$_2$ strongly favor V$_0$ over O$_0$. (The above conclusion is reasonable in view of the different crystal structures of Y$_2$O$_3$ and fluoric-structured oxides, especially the existence of missing oxygens in the former as shown in Fig. 1.) This could also imply that at grain boundaries, where defect equilibrium is presumably maintained, the relative population of V$_0$ and O$_0$ would be similar in Y$_2$O$_3$ but would be richer in V$_0$ in CeO$_2$ and ZrO$_2$. If so, we may further speculate on a more stoichiometric composition at the grain boundary in Y$_2$O$_3$ compared to CeO$_2$ and ZrO$_2$, which, in turn, could cause a lower grain boundary diffusivity in Y$_2$O$_3$.

VII. Conclusions

(1) In Y$_2$O$_3$, grain boundary mobility is controlled by cation diffusivity, and cations diffuse by an interstitial mechanism that can be enhanced by the presence of oxygen vacancies and suppressed by the presence of oxygen interstitials.

(2) Acceptor dopants, which introduce oxygen vacancies, enhance the grain boundary mobility. Donor dopants, which introduce oxygen interstitials, suppress the grain boundary mobility. Overall, Sr$^{2+}$ increases grain boundary mobility the most and Zr$^{4+}$ decreases grain boundary mobility the most.

![Fig. 10. Schematic for solute effect on grain boundary mobility.](image)

![Fig. 11. Grain boundary mobility of CeO$_2$, Y$_2$O$_3$, and ZrO$_2$ systems.](image)
(3) The anomalous effect of undersized dopants (Ti and Nb) on enhancing grain boundary mobility cannot be explained in terms of valence alone, but is likely due to lattice distortion, which is consistent with similar findings in CeO₂.

(4) Activation energies of grain boundary mobility vary from 0.67 eV (Zr doping) to 2.8 eV (Mg doping), indicating a very strong binding energy between dopants and oxygen defects.

(5) Cation migration via an interstitial mechanism is suggested to be a general mechanism that dominates diffusive processes in fluorite and modified fluorite-structured oxides such as CeO₂, UO₂, ZrO₂, Y₂O₃, and cubic Bi₂O₃.

**APPENDIX**

**Defect Concentration and Grain Boundary Mobility**

The concentration of effective oxygen vacancy as a function of temperature in the presence of acceptor dopant is calculated by the following equation:

\[
[V_{O}]_{\text{eff}} = \frac{[D_a]}{1 + A_a \exp(B_a/kT)}
\]

(A-1)

where \([D_a]\) is the concentration of acceptor dopant, \(A_a\) is 6.76 × 10⁻¹⁴, \(B_a\) is the binding energy between acceptor dopant and oxygen vacancy, which is 5 eV, and \(kT\) has its usual meaning. Further, the grain boundary mobility of Y₂O₃ with acceptor dopant can be obtained by

\[
M_a = \left( \frac{[V_{O}]_{\text{eff}}}{[V_{O}]_{\text{intrinsic}}} \right)^{1.5} M_Y
\]

(A-2)

where \([V_{O}]_{\text{intrinsic}}\) is the concentration of intrinsic oxygen vacancy, and \(M_Y\) is the grain boundary mobility of undoped Y₂O₃.

Similarly, the concentration of effective oxygen interstitial and the grain boundary mobility of Y₂O₃ doped with donor dopant can be obtained from the following equations:

\[
[V_{I}]_{\text{eff}} = \frac{[D_d]}{1 + A_d \exp(B_d/kT)}
\]

(A-3)

\[
M_I = \left( \frac{[V_{I}]_{\text{intrinsic}}}{[V_{I}]_{\text{eff}}} \right)^{1.5} M_Y
\]

(A-4)

where \([D_d]\) is the concentration of donor dopant, \(A_d\) is 1.833 × 10⁻¹³, \(B_d\) is the binding energy between donor dopant and oxygen interstitial, which is 5 eV, \([V_{I}]_{\text{intrinsic}}\) is the concentration of intrinsic oxygen interstitial, and \(M_I\) is the grain boundary mobility of Y₂O₃ doped with donor dopant. As shown in Fig. A1, the grain boundary mobility of Y₂O₃ doped with either acceptor or donor dopant can be shown to agree with the above calculation.

**References**


W. Y. Ching: private communication.

