Bulk Diffusion in Alumina: Solving the Corundum Conundrum

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Outline



Introduction

- Intrinsic defects in Alumina
- Doping and Clusters
- Diffusion in Alumina
- Defect Formation Energies
- 2 Defect Concentrations in Alumina
 - Defect Formation Energies
 - Self-Consistency
- 3 Diffusion Coefficients
 - Migration Barriers
 - Calculating Diffusion Coefficients
 - Effects of Aliovalent Doping



Intrinsic defects in Alumina Doping and Clusters Diffusion in Alumina Defect Formation Energies

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Summary

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Alumina

$\alpha\text{-Al}_2\text{O}_3\text{:}$ Corundum Structure (2:3 coordination \Rightarrow 1/3 Al sites vacant).





Traditionally thought of as fully ionic: $(AI^{3+})_2(O^{2-})_3$. Large band gap, fully occupied O 2*p* bands, empty Al 3*s*/3*p* bands.

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Point Defects

Intrinsic defects in Alumina Doping and Clusters Diffusion in Alumina Defect Formation Energies

Ceramic crystals formed and annealed at high temperatures always contain nonzero concentrations of intrinsic point defects, even when 'pure'

$$V_0, V_{AI}, O_i, AI_i, \dots$$
 (1)

Concentrations of defects depend on annealing conditions, p_{O_2} , T.

Equilibrium concentrations minimise total Gibbs Free Energy G subject to constraints of charge neutrality and particle number.

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Point Defects

Alumina is the 'prototypical' refractory ceramic. Properties as a refractory oxide strongly depend on defects and their diffusion coefficients:

- Electrical Conductivity
- Grain Growth
- Plastic Deformation
- Oxide film growth
- Sintering, Creep



Intrinsic defects in Alumina

N.D.M. Hine Bulk Diffusion i

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Point Defects

Intrinsic defect population in pure alumina can only form charge neutral combinations. In traditional, fully-ionic picture these are:

Schottky (vacancies) and anti-Schottky (interstitials)

$$3V_0^{2+} + 2V_{AI}^{3-}$$
 and $3AI_i^{3+} + 2O_i^{2-}$ (2)

Cation Frenkel (Al ions) and Anion Frenkel (O ions)

$$V_{AI}^{3-} + AI_i^{3+}$$
 and $V_0^{2+} + O_i^{2-}$ (3)

In these combinations, variations in atom chemical potentials due to annealing conditions also cancel, since formation energies contain zero net contribution from μ_{AI} and μ_{O} (NB $2\mu_{AI} + 3\mu_{O} = \mu_{AI_2O_3}$)

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Doping

- Aliovalent dopants (eg Mg and Ti) affect balance of charge:
- e.g. Replace neutral trivalent Al atom with neutral tetravalent Ti.
- 3 valence electrons from Ti_{AI} complete 2p shells of nearby O^{2-} .

One valence electron would remain in Ti 4s defect state below conduction band edge (6-8 eV above VBM).

System can lower free energy by creating a -ve point defect and transferring electron to this.

 \Rightarrow Ti_AI is source of electrons & prompts formation of -ve defects.

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Doping

Likewise, divalent Mg_{AI} only donates 2 electrons and thus requires an extra electron to come in from elsewhere to fill O 2*p* shells of neighbours.

 \Rightarrow Mg_{AI} is acceptor of electrons & prompts formation of +ve defects?

Remember that the O 2p hole is *above* top of VBM so filling depends on Fermi energy.

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Clusters

Substitutional impurity and intrinsic defect have opposite charge and may *bind* to form defect clusters, such as

$$(Ti_{AI} : V_{AI})^{2-}$$
 and $(Mg_{AI} : V_0)^{1+}$ (4)

However, even though Δg_f for the reaction is usually -ve, entropy may outweigh it at finite $T \Rightarrow$ Clusters dissociate at high temperatures.

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Intrinsic defects in Alumina Doping and Clusters **Diffusion in Alumina** Defect Formation Energies

Point Defect Concentration and Migration

Law of Mass Action gives concentrations c_i of each species in terms of formation energy ΔG_i^f per defect:

 $c_i = m_i e^{-\Delta G_i^f / kT}$

Formation energies also determine diffusion coefficients by Arrhenius Equation

$$D_i = D_i^0 e^{-E_i^a/kT}$$

where activation energy $E_i^a = \Delta G_i^f + \Delta G_i^b$, where ΔG_i^b is the migration barrier between adjacent equivalent positions of the defect.

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Intrinsic defects in Alumina Doping and Clusters **Diffusion in Alumina** Defect Formation Energies

The Corundum "Conundrum"

Despite widespread industrial usage, defect phenomena in AI_2O_3 not well-understood or well-controlled.

Diffusion experiments are our only experimental window to understanding, but low intrinsic concentrations, lack of good radiotracer for Al, and unknown impurities content of samples limit interpretation of results.

Previous Classical Potential and DFT calculations produced formation energies very hard to reconcile with experiment $(E_a \sim 6 \text{eV})$.



Temperature (°C)

Figure 1. Oxygen diffusion data for undoped, MgO-doped and TiO:-doped a-Al:O: from Lageriol et al. (1989), together with data for undoped a-Al:O: from others in the period 1980–1996. See text for further details.

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Intrinsic defects in Alumina Doping and Clusters **Diffusion in Alumina** Defect Formation Energies

The Corundum "Conundrum"

Some clear facts emerge from experiments

- D_{O} is *smaller* than D_{AI} (or D for cation impurities) by several orders of magnitude
- Rate-limiting $D_{\rm loop}$ sensitive to balance of aliovalent impurities. Up by \sim 100 with 250ppm Mg; down by \sim 50 60 with 600ppm Ti.
- However, given very low intrinsic concentrations $\sim 10^{-10},$ these are remarkably small changes

Could native defect concentrations somehow be "buffered" against increasing concentrations of dopants? What role do defect clusters play? Can we predict diffusion coefficients *ab initio*?

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Formation Energies

However ΔG_i^f depends on chemical potentials of species transferred to and from 'reservoirs' to create defect *i*:

$$\Delta G_i^f = G_i^{\text{def}} - \sum_{\alpha} (n^{\alpha} + \Delta n_i^{\alpha}) \mu_{\alpha} + q_i \mu_e$$

 G_i^{def} : Gibbs energy of supercell with defect *i*, charge q_i . μ_e, μ_α : chemical potential of electrons & atom species α

$$\Delta G_i^f = G_i^{\text{def}} - G_i^{\text{perf}} - \sum_{\alpha} \Delta n_i^{\alpha} \mu_{\alpha} + q_i \mu_e$$

 G_{i}^{perf} : Total energy of supercell of perfect crystal = $\sum_{lpha} n^{lpha} \mu_{lpha}$

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Formation Energies

So, each ΔG_i^f , and thus the c_i 's depend on μ_e , μ_O and μ_{AI} .

 μ_{O} and μ_{Al} are functions of annealing conditions: Determine via combination of Ideal Gas Eq for $\mu_{\frac{1}{2}O_2(g)}$ at T, $p_{O_2(g)}$, and experimental and theoretical values for $\Delta G_f(Al_2O_3)$ (see work of Finnis, Lozovoi, Alavi — another story).

Creating more charged defects (or introducing aliovalent dopants) affects Fermi energy.

 \Rightarrow Need to *Self-Consistently* determine $\mu_e!$

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Intrinsic defects in Alumina Doping and Clusters Diffusion in Alumina Defect Formation Energies

Grand Canonical Minimisation

We can see that

- Concentrations sum to 1: $\sum_i c_i = 1$.
- Total charge is $Q = \sum_i c_i q_i$.
- Total number of Mg atoms is $\sum_i c_i \Delta n_i^{Mg}$.
- Total number of Ti atoms is $\sum_i c_i \Delta n_i^{\text{Ti}}$.

Obtain c_i 's that minimise G, subject to constraints:

- Overall charge neutrality Q = 0
- Target level of Mg doping $\sum_i c_i \Delta n_i^{Mg} = [Mg]$
- or Target level of Ti doping $\sum_i c_i \Delta n_i^{Ti} = [Ti]$

Transforms chemical potentials $\mu_{\rm e}$, $\mu_{\rm Mg}$, and $\mu_{\rm Ti}$ into Lagrange Multipliers.

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Intrinsic defects in Alumina Doping and Clusters Diffusion in Alumina Defect Formation Energies

Grand Canonical Minimisation

Total Gibbs Free Energy G of system of N unit cells is

$$G = N \left\{ \sum_{i=0}^{I} c_i g_i + k_B T \sum_{i=0}^{I} c_i \ln(c_i/m_i) \right\}$$
(5)

• c_i: Concentration of cells containing defect of type i

- g_i: Gibbs energy of cell containing defect of type i
- *m_i*: Multiplicity of defect type *i*.

Minimise G w.r.t. N and the c_i 's subject to constraints

 \Rightarrow *I* + 1 equations, *I* + 1 unknowns

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Cluster Mass Action

Can also obtain Law of Mass Action for formation of clusters, eg for

$$Mg_{AI}^{1-} + V_O^{2+} \Leftrightarrow (Mg_{AI} : V_O)^{1+}$$
(6)

we get

$$\frac{[Mg_{A|}^{1-}][V_{O}^{2+}]}{[(Mg_{A|}:V_{O})^{1+}]} = k_{0}e^{\Delta g_{f}/kT}$$
(7)

where k_0 is the ratio of multiplicities of each defect. Hence

$$[(Mg_{AI}: V_{O})^{1+}] = \frac{1}{k_{0}} e^{-\Delta g_{f}/kT} [Mg_{AI}^{1-}] [V_{O}^{2+}]$$
(8)

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Defect Formation Energies Self-Consistency

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Defect Formation Energies Self-Consistency

Methods

Calculate formation energies of lots of defects!

- Plane wave DFT with CASTEP.
- LDA (+PBE for comparison), USP's, 550eV PW cutoff.
- Full geometry relaxation of each structure.
- Finite Size extrapolation to infinite dilution limit (120-540 atom cells).
- FLA approach to chemical potentials.
- No 'band-gap' corrections.
- DFPT with harmonic approximation for $\Delta g(T)$ for each cell.

For more details see N.D.M Hine, K. Frensch, W.M.C. Foulkes, and M.W. Finnis, Supercell size scaling of density

functional theory formation energies of charged defects, Phys. Rev. B 79, 024112 (2009).

Defect Formation Energies Self-Consistency

Formation Energies

First step is to calculated defect formation energies *parameterised* by μ_e , μ_{α} for all possible contributing species:

$$\Delta G_i^f = G_i^{\text{def}} - G_i^{\text{perf}} - \sum_{\alpha} \Delta n_i^{\alpha} \mu_{\alpha} + q_i \mu_{\epsilon}$$



NB: Most papers stop here! But no use to experimentalists yet..._

Defect Formation Energies Self-Consistency

Cluster Binding Energies

Binding energies of several significant cluster species:

Cluster Species	Δg_f (eV)
$(Mg_{AI}:V_O)^{1+}$	3.56
$(Ti_{AI} : V_{AI})^{2-}$	2.56
$(Mg_{AI} : AI_i^{2+})$	3.67
$(2 T_{AI} : V_{AI})^{1-}$	3.67
V ¹⁻ _{AlO}	3.06

 V_{AIO}^{1-} may have a significant intrinsic population...

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Defect Formation Energies Self-Consistency

Self-Consistent Concentrations

Algorithm

- Specify q_i , m_i , Δn_i^{α} for each defect
- Input $\Delta G_i^f(T)$ for each defect
- Specify $\mu_{\rm AI}$ and $\mu_{\rm O}$ from external conditions, T, $p_{\rm O_2}$.
- Provide initial guesses for μ_e (Valence Band Maximum) and μ_{Mg} ($E_T(Mg_s)$)
- Loop over μ_e in the range E_{VBM} to E_{CBM} .
- Loop over μ_{Ti}
- Calculate ΔG_i^f and hence c_i for each defect.
- Calculate $Q = \sum_i c_i q_i$, $[Mg] = \sum_i c_i \Delta n_i^{Mg}$.
- Stop if Q = 0 and $[Mg] = [Mg]_{targ}$. Record final c_i 's and μ_e .

Very easy to code and fast to implement

Defect Formation Energies Self-Consistency

Self-Consistent Concentrations

Concentrations of substitutionals with increasing doping



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Defect Formation Energies Self-Consistency

Self-Consistent Concentrations

Concentrations of substitutionals, vacancies and clusters



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Defect Formation Energies Self-Consistency

Self-Consistent Concentrations

Concentrations of all significan defects, and Fermi level



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Defect Formation Energies Self-Consistency

Buffering Explained

Recall that

 $[(Mg_{AI}: V_{O})^{1+}] = \frac{1}{k_{0}} e^{-\Delta g_{f}/kT} [Mg_{AI}^{1-}] [V_{O}^{2+}]$ (9)

Overall [Mg]	[V _{AI} ³⁻]	[V ₀ ²⁺]	[Mg ¹⁻]	$[(Mg_{AI} : V_O)^{1+}]$	ϵ_F
Undoped	const [V ³⁻] _µ	const $[V_0^{2+}]_u$	near zero	near zero	stable
Low	const $[V_{AI}^{3-}]_u + \delta$	const $[V_0^{2+}]_u - \delta$	rising \propto [Mg]	rising \propto [Mg]	stable
Intermediate	falling \propto [Mg] ⁻¹	rising \propto [Mg]	rising \propto [Mg]	rising \propto [Mg] ²	falling
High	const ~ 0	const [V _O ²⁺] _f	rising \propto [Mg]	rising \propto [Mg]	stable

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Migration Barriers Calculating Diffusion Coefficients Effects of Aliovalent Doping

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Migration Barriers Calculating Diffusion Coefficients Effects of Aliovalent Doping

DFT Migration Barriers

Move atoms step by step from one possible site to an adjacent one

Constrain atom to series of planes perpendicular to vector joining start and end points.

Relax all atoms fully at each fraction along vector.



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Migration Barriers Calculating Diffusion Coefficients Effects of Aliovalent Doping

DFT Migration Barriers

Migration barriers to site-to-site diffusion of oxygen vacancy

Different paths show very different barriers.

Lowest barriers \sim 1eV only permits movement around smaller triangles of O²⁻ ions. Real barrier to 3D diffusion is \sim 1.73eV.

Oxygen Vacancy Migration Barrier



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Migration Barriers Calculating Diffusion Coefficients Effects of Aliovalent Doping

DFT Migration Barriers

Migration barriers to site-to-site diffusion of aluminium vacancy

Revealed a whole new unexpected configuration (of notably lower energy)

Split vacancy along *c*-axis.



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Migration Barriers Calculating Diffusion Coefficients Effects of Aliovalent Doping

Split Aluminium Vacancy

Can be thought of as 2 vacancies and 1 interstitial...







Migration Barriers Calculating Diffusion Coefficients Effects of Aliovalent Doping

Split Aluminium Vacancy Migration

Moves in complex correlated motion of several atoms.





Overall barrier is relatively low.

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Migration Barriers Calculating Diffusion Coefficients Effects of Aliovalent Doping

Migration Barriers

Summary of migration barriers for intrinsic defect species:

Defect Species	$\Delta E_{\rm mig}$ (eV)	
V ₀ ²⁺	1.73	
V _{AI} ³⁻	1.27	
Ali ³⁺	1.31	
O _i 1-	0.69	
V _{AIO} ¹⁻	2.35	

Reasonably in line with expectations of ceramicists (much lower than previous estimates — which presumably did not find the fully relaxed path)

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Migration Barriers Calculating Diffusion Coefficients Effects of Aliovalent Doping

Calculating Diffusion Coefficients

Diffusion coefficients D_i given by Arrhenius equation:

$$D_i = D_0 e^{-E_i^a/k_{\rm B}T},$$
 (10)

where the activation energy E_i^a is the sum of the migration energy and the formation energy.

Pre-exponential factor $D_0 \propto f \alpha^2 \nu$,

- f: correlation factor (calculate from structure)
- α : jump distance (estimate from bond lengths)
- ν : attempt frequency (estimate from phonon frequencies)

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Migration Barriers Calculating Diffusion Coefficients Effects of Aliovalent Doping

Reliable Experimental Diffusion Measurements

Loop annealing Data (Heuer), Al Tracer data (Fielitz)



Reciprocal Temperature (104/K)

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Migration Barriers Calculating Diffusion Coefficients Effects of Aliovalent Doping

Oxygen Diffusion Coefficients

Calculated vs Experimental diffusion coefficients for V_0 .



Reciprocal Temperature (104/K)

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Migration Barriers Calculating Diffusion Coefficients Effects of Aliovalent Doping

Aluminium Diffusion Coefficients

Calculated vs Experimental diffusion coefficients for V_{AI} and AI_i .



Reciprocal Temperature (104/K)

Image: A image: A

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Migration Barriers Calculating Diffusion Coefficients Effects of Aliovalent Doping

Conundrum Solved?

'Buffering' effect observed under aliovalent doping in oxygen and aluminium diffusion coefficient explained in terms of movement of Fermi level with changing ratios of concentrations of substitutionals relative to intrinsic defects and clusters.

Predicted and observed activation energies reconciled: good quantitative predictions of diffusion coefficients made possible in ceramics.

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- A new approach to *Self-Consistent* determination of defect concentrations and diffusion coefficients.
- Explains the long-standing mysteries of diffusion in Alumina.
- Ab Initio calculations of diffusion coefficients agree well with experiments (to 1-2 orders of magnitude).

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Outlook

- Other common dopants? Cr, Fe? (requires some treatment of correlated *d*-electrons)
- Ever larger clusters & larger supercells (towards ONETEP regime)
- Solubilities work in progress (KF)
- Did we get the right structure for all defects? (esp O_i)
- Can we do Grain Boundaries rich, interesting, unexplained physics
- Opens up diffusion in ceramics to the same kind of "engineering" of desired properties possible with doping in semiconductors.

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