Theory of Diffusion and Aggregation of Radiation-Induced Defects in MgO and α-Al₂O₃ Crystals

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Abstract: This paper describes three separate-but related-investigations of defects in the technologically important ceramics MgO and α-Al₂O₃. We used several different but complementary theoretical techniques. Pair-potential methods are well-suited to the calculation of defect energies of formation, aggregation and migration when no charge re-distribution occurs. CNDO or INDO semi-empirical methods must be used for very large clusters or unit cells containing hundreds of atoms. First-principles methods like Hartree-Fock and density-functional theory schemes are appropriate for small unit cells containing up to 16 or 32 atoms. Here the use of these methods for isolated defects and clusters in MgO and corundum, and for oxygen atom interstitials in MgO is discussed.

Pair-potential and INDO Calculations: α-Al₂O₃ (corundum) and MgO are important ceramic materials with several technological applications including their possible use in fusion reactors [1]. In unirradiated materials with the rock-salt structure Schottky defects usually predominate and this proves to be so also in MgO. In corundum Schottky defects are marginally favoured over anion Frenkel defects. For both these materials pair-potential (PP) calculations were carried out using the Mott-Littleton strategy as implemented in the computer code CASCADE due to Leslie [2]. Details of the method, including the evaluation of short-range forces, are given in [3] and references therein. In semi-empirical INDO (intermediate neglect of differential overlap) calculations, two computer codes developed at the University of Riga were used [4, 5]. Defect formation energies are given in Table 1 and the favoured migration energies in Table 2 [6, 7]. For MgO the calculated defect energies suggest a vacancy mechanism for both anion and cation diffusion with Arrhenius energies of 6.0 and 5.9 eV respectively, the former result being in reasonable agreement with the experimental value of Oishi and Ando [8] of 6.5 eV for intrinsic oxygen diffusion. The experimental migration energies for O vacancy diffusion vary from 2.03 ± 0.17 eV [1] to 2.7eV [8], both PP and INDO calculations fall within this rather wide range. For Mg diffusion Sempolinski and Kingery [9] and Duclot and Departes [10] found activation energies of 2.3 ± 0.2 eV, and 2.2 eV respectively, which are slightly greater than our calculated value of 1.98 eV. Isotropic diffusion of oxygen in corundum requires a succession of a1 and a3 hops; the rate-determining step is a3, and our calculated value of 1.85 eV is in good agreement with the experimental value of Oishi [8] of 1.86 eV. In MgO there is no reason to suspect non-linear migration paths but in the rhombohedral unit cell of corundum asymmetric Coulomb interactions favour a curved diffusion path for a1. The minimum energy trajectory deviates from a linear path by $\Delta = 0.34$ Å. INDO calculations of vacancy migration confirmed this, yielding values of $\Delta = 0.42$Å and $E = 0.49$ eV, in quite reasonable agreement with our PP calculations.

Table 1   Defect formation energies (in eV) *per defect*, for MgO and α-Al$_2$O$_3$ calculated by the pair-potentials method.

	MgO	α-Al$_2$O$_3$
Schottky	3.89	4.91
anion Frenkel	6.17	5.13
cation Frenkel	6.25	6.43

Table 2.   Activation energies (in eV) for the migration of vacancies (*v*) in MgO and α-Al$_2$O$_3$ and of interstitials (*i*) in MgO. *a* = anion, *c* = cation, *ic* = interstitialcy collinear, a1 = shortest path between anions in small triangles in planes $\perp$ **c** axis; a3= jump along **c** axis from small to large triangles $\perp$ **c**; c4 = path between cation sites in adjacent c-axis stacks. (A diagram of the rhombohedral unit cell of corundum is in ref. [11]).

	MgO			α - Al$_2$O$_3$ [6, 11]	
	PP[12]	INDO[7]		PP	INDO
av	2.09	2.50	a1	0.34	0.49
cv	1.98	2.43	a3	1.85	-
aic	0.54				
cic	0.43		c4	3.76	-

The INDO calculations confirm that negligible charge re-distribution occurs in the oxygen saddle point, as is assumed in PP calculations. Calculations on the stability of cation or anion Frenkel pairs in MgO when *a* and *c* are in close proximity demonstrate that fourth nearest neighbour (4nn) Frenkel pairs are stable but closer pairs are unstable. This means that with an *i* at (-½ , -½, - ½), the closest stable position for *v* is (1, 1, 1). Thus we can expect stable *i* and *v* to be formed in high local concentration during irradiation, with consequent clustering. Some cluster energies are in Table 3 [12]. These clusters are seen to be remarkably stable. The vacancy and interstitial quartets provide possible mechanisms for the nucleation of bubbles and dislocations loops [1].

Table 3.   Defect cluster energies (in eV) in MgO. F = Frenkel pair, vp = vacancy pair.

Cluster	Energy	with respect to :
4nn, a F	-0.82	separated species
4nn, cF	-0.84	separated species
nn, ai+ci dimer	-5.35	separated ai, ci
i quartet (2 nn dimers)	-0.97	separated dimers
nn vp	-2.72	separated cv, av
nn vacancy quartet	-3.04	2 separated vp

Oxygen Atom Interstitials in MgO   Irradiation of MgO produces F centres and therefore O atoms [13]. However, little was known about the fate of these O atoms until recently when two parallel, but independent, investigations [14,15] revealed that an interstitial O atom in MgO combines with a lattice O^{2-} ion to form a symmetrical O ˙ - O ˙ 'dumbbell' centred on a lattice site. However, a fundamental difference in the results was that the former investigation [14] of Brudevoll et al. predicted that the stable position for the dumbbell was along <111> while the latter one [15] of Evarestov et al. gave the most stable configuration along <110>. Brudevoll et al. [11] used a full-potential linear-muffin-tin-orbital method (LMTO-LDA) [16] whereas Evarestov et al. used a periodic Hartree-Fock self-consistent field (HF) large unit cell (LUC) method [17]. A significant difference between the two investigations was that in [14] the LUC or supercell used contained 8 primitive unit cells (S8) whereas in [15] S16 supercells were used. Furthermore, Evarestov et al. [15] used a CNDO method to verify that neither the charge distribution nor the defect levels in the band gap changed significantly as the size of the supercell increased from S16 to S32, S64 and S128. It became a major concern to both groups to resolve this discrepancy and especially whether it arose from a fundamental difference between the LMTO and HF methods or was just an artefact due to the differences in supercell size. Accordingly, the HF calculations were repeated using S8 supercells, paying very careful attention to the lattice relaxation. No automated way currently exists to do this and accordingly the ion positions must be relaxed 'by hand'. Results of the HF and LMTO-LDA procedures for S8 are summarized in Table 4.

Table 4   Energy (in eV) of the oxygen atom interstitial in MgO in various configurations: v= volume-centred, f= face-centred, d=dumbbell, n denotes the relaxation of all symmetry-related near-neighbour ions that lie completely within the supercell. D is the distance between the centres of the two atoms in a dumbbell in Å. Defect energies are given with respect to the ground state, vdn.

Defect	E/eV		D/Å	
	HF	LMTO-LDA	HF	LMTO-LDA
vn	12.25	3.57		
fn	2.30	1.45		
fd	1.96		1.328	
vd	1.08		1.364	
fdn	0.09	0.15	1.380	1.375
vdn	0	0	1.390	1.364

Both calculations predict that the dumbbell is the stable configuration, with the calculated D values agreeing to better than 2%; and they agree that (in S8) vdn lies below fdn. The defect energies relative to vdn are qualitatively similar, except for vn where the HF value is much larger than the LMTO one. The atomic coordinates for the relaxed v, f, vd and fd configurations determined by the two methods are in excellent agreement. Since these calculations were carried out completely independently it appears

that the same energy minima have been located, and that the energy differences are due to the difference in the methods employed. To put these differences in perspective, one should recall that the HF energy of vdn in the S8 supercell is -2272.9415 H, so that the worst difference of 8.67 eV amounts to 0.014 %! So at this defect concentration one may say that the LMTO-LDA and HF calculations agree in their predictions. However, one must use a larger supercell (S16) to determine the ground state more precisely [18] since the second-neighbour O atoms may not relax in S8. Our calculations show that the mechanism of O_i atom diffusion in irradiated MgO involves these dumbbells. There are two possibilities: the HF S16 calculations [18] suggest a <110> motion of O_i along cube-faces with an activation energy E=2.00 eV, whereas the LMTO-LDA (S8) calculations [14] suggest a rotation of <111> dumbbells vdn to fdn, with O_i atom hopping along <110>, for which the calculated E of 1.45 eV. These values bracket the experimental activation energy of 1.6 eV found for diffusion-controlled recombination of O-related defects during annealing of irradiated MgO [13]. The fact that the dumbbell is accommodated so readily in the MgO lattice seems to be the reason why no appreciable volume change occurs in MgO during irradiation [13]. Both sets of calculations agree that neutral O_i atoms produced during irradiation immediately combine with nn O^{2-} ions to form O^- - O^- dumbbells which are the stable species.

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