Computer Modelling of Radiation Damage in Cation Sublattice of Corundum

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Results of quantum chemical computer simulations of close Frenkel defects in corundum crystals are presented and discussed. The conclusion is drawn that the energy barrier for a back recombination up to fourth nearest neighbours is less than 0.3 eV, i.e. such pairs should be unstable at temperatures above 40 K.

1. Introduction

Single crystals of corundum (α-Al_2O_3) having a unique combination of physico-chemical and technological properties are of great interest for different applications including solid state lasers, dosimetry, microelectronics and nuclear fusion reactors. Radiation-induced defects (colour centres) created by electrons, neutrons, and ion irradiation in α-Al_2O_3 have been intensively studied during the last three decades which led to a considerable progress in the characterization of the point defects therein. As a result of experimental and theoretical studies [1 to 4], the identification of anion intrinsic defects (the F^+, F, F_2, F_2^+ and F_2^{2+} centres) and cation defects (V^-, V^{2-} centres) in Al_2O_3 is on firm footing. The V^- and V^{2-} centres are formed by trapping of positive holes by cation vacancies. Their complementary Frenkel defects are interstitial Al_i atoms.

It is well established that in α-Al_2O_3 new vacancies and interstitials are created by elastic collisions. The efficiency depends on the kind of sublattice, i.e. the displacement energies for oxygen and aluminium are quite different (cf. experimental estimates of 75 [5], 76 [6], 79 eV [7] for O and 18 [5, 6] to 24 eV [7] for Al). This asymmetry is in agreement with recent theoretical studies [8] and means that there is more primary displacement on the cation sublattice than on the anion one. However, the actual number of stable defects in each sublattice depends on secondary processes in the collision cascade and on the way defects are stabilized. At the beginning of the 60s, studying the absorption spectra of neutron-irradiated Al_2O_3, Levy [9] has noted that the intensity of all produced absorption bands, taken singularly or together, was significantly less than implied by the concentration of radiation-induced point defects expected on the basis of the Kinchin-Pease theory. The latter claims that about 90% of defects produced by collision events anneal out immediately while the rest survives. The comparison of the observed number of oxygen vacancy centres (F and F^+) [10, 11] with collision calculations gives a concentration ratio of only 0.035 [12]. In a recent paper Zinkle [13] has analyzed the measurements of the surviving defect fraction in Al_2O_3 [14 to 18] and

bulk Al [19] as a function of the average primary energy of knock-on atoms. He concluded that the low measured surviving defect fraction at low energies could be associated with ionization-induced migration and recombination of point defects. Thus, both recombination of complementary Frenkel defects (called also *geminate*) which are usually well-correlated in space at the moment of creation, and recombination of well-separated (spatially uncorrelated) dissimilar point defects due to their diffusion affect the concentration of *stable* intrinsic point defects and result in its overestimation in theoretical calculations.

Careful analysis of experiments is complicated by a lack of information on interstitial migration energies and stability of close Frenkel pairs in Al_2O_3. Also, very little is still known about interstitial aluminium atoms, Al_i, which are complementary defects to cation vacancies. One possible reason for the paucity of experimental evidence for the interstitials is that, as such, they may be unstable already at moderate temperatures (this is the case for anion interstitials, I centres, in alkali halides [20]). Indeed, as it was mentioned by Zinkle [13], several studies suggest that interstitials in Al_2O_3 may be mobile at temperatures below 80 K (the corresponding activation energies vary from 0.2 to 0.8 eV) [14, 21], whereas other authors concluded that interstitials migrate only at temperatures above 300 K with migration energies as high as 1.8 eV [16, 22]. In particular, Cox [21] has found at least two ESR resonances in neutron-irradiated Al_2O_3 at 77 K which he attributed to Al_i complexes, comprising an Al^{3+} ion in a regular lattice site and an interstitial Al^{2+} ion, which demonstrates the high mobility of Al interstitials. On the other hand, Agnew [16] and Pells [23] claim that defects in the aluminium sublattice are stable up to 400 °C, since above this temperature the V centres begin to anneal out and this process has nothing to do with the mobility of their complementary Al_i defects, as well as with the mobility of cation vacancies. Last, Pells and Shikawa [24] have observed the formation of aluminium precipitates formed by the trapping of migrating interstitials at void surfaces and found an activation energy of 1.35 eV, which was ascribed to Al_i motion. However, this assignment is not obvious. The main problem to be addressed in this paper is the calculation of the formation energies and the stability of close Frenkel defects in the aluminum sublattice.

2. Method

For this purpose a relatively simple theoretical approach is needed allowing us to study large quantum clusters (about 100 to 200 atoms) and complex defects (Frenkel pairs at different separations), to be able to optimize the defect geometry through a minimization of the total energy, and to model defect diffusion hops. Such an approach to large-scale simulations of static and dynamical properties of defects in ionic solids has been elaborated in recent years on the basis of the semi-empirical quantum chemical method, Intermediate Neglect of Differential Overlap (INDO) [25]. The original calculation and parametrization scheme was considerably modified (see more in [26]. This new method has been applied very successfully to the study of defects in many oxide materials, including MgO, SiO_2, Li_2O, ZrO_2, TiO_2, α-Al_2O_3 etc. The INDO method is based on a Hartree-Fock-type formalism and allows self-consistent calculations of the atomic and electronic structure of point defects and the position of defect levels with respect to the perfect crystal energy bands, as well as the electronic density/spin distribution. This method permits easy calculations of both clusters and periodic defects using the so-

called large unit cell model (SYM-SYM) code [27, 28]. Recently, we performed a number of INDO calculations for the optical properties of electron and hole centers in corundum [28 to 30]. These papers give details on the method and basis set used.

In this paper, we performed semi-empirical INDO cluster calculations for the primary Frenkel defects in the cation sublattice of corundum crystals using a 130-atom stoichiometric cluster which contains 26 structural elements, Al_2O_3. The V_{Al} and Al_i radiation defects form a sequence of close Frenkel pairs ranging from 1NN to 4NN (the relative distances are 1.73, 2.53, 3.36 and 4.69 Å, respectively). It should be remembered that the corundum structure could be viewed as hexagonal close packing of O atoms with Al atoms occupying 2/3 of octahedral interstices. In our simulations we assume that Al atoms are removed from their regular lattice sites and placed on these empty interstitial positions. The lattice relaxation of several spheres of surrounding atoms is calculated. The automated procedure for lattice geometry optimization around a defect is described in detail in [3]. To calculate the total energy surface, we also applied this procedure for a large number of points connecting initial and final positions of the Al_i atom (its coordinates were fixed each time), including nonlinear routes for far lying neighbours. Hereafter, we call the *net formation energy* the difference in total energy minimum for a cluster with interstitial aluminium atoms in the relaxed 1 to 4 NN position and the perfect cluster energy. The experimentally observed threshold energy is the sum of the defect net formation energy and the *recombination barrier* energy.

3. Results and Discussion

The main results obtained are given in Table 1. It is demonstrated that:

(i) NN pairs are unstable and recombine immediately. The formation energy for the 2NN to 4NN pairs increases from 15.9 to 26 eV. This is in good agreement with experimental estimates ranging between 18 and 24 eV [5 to 7].

(ii) Neglecting the ionic relaxation increases the formation energy for 3NN up to 32 eV.

(iii) The barrier energy for Al_i back recombination even for 4 NN is small and could be estimated as 0.3 eV. In other words, the first four kinds of Frenkel defects are unstable at moderate temperatures since Al_i becomes highly mobile around liquid nitrogen temperature.

(iv) The activation energy for *free* Al_i diffusion is about 0.3 to 0.4 eV, in complete agreement with the analysis cited above, indicating high mobility of interstitial aluminium atoms [13].

Table 1

Calculated formation energy of close cation Frenkel pairs and initial/final equilibrium coordinates of Al_i atoms displaced to the octahedral interstitial position with coordinates $(0, 0, 0)$ in a perfect crystal

type of pairs (nearest neighbours)	initial Al coordinates (at. units)	final Al coordinates (at. units)	formation energy (eV)	recombination barrier (eV)
1NN	(0, 0, 3.27)	(0, 0, 0)	15.2	0
2NN	(−4.76, 0, 0.45)	(−1.12, 0.06, 0.08)	15.9	0.26
3NN	(−4.76, 0, −4.22)	(−0.5, 0.04, 0.06)	20.1	0.28
4NN	(7.14, −4.12, 3.27)	(0.03, −0.02, 0)	26.0	0.30

(v) Last, in the interstitial position Al_i attracts considerable electron density from nearest O ions. Thus, in the 3NN position its effective charge is just $0.63e$, to be compared with $2.42e$ for a regular Al ion in a corundum lattice site. This demonstrates that use of the atom–atom potential approach could be problematic in corundum simulations where a self-consistent quantum chemical formalism is more adequate. This could be the reason why in a recent study [8] the formation energy for well-separated cation Frenkel pairs exceeds twice the experimental value. A more striking example is the Al migration energy found in [31] to be 5 eV − an order of magnitude overestimation.

The high mobility of cation interstitials is also confirmed by the experimental results on both MgO [32] and Al_2O_3 [33] where under low-temperature neutron irradiation, the optical absorption bands associated with anion vacancies are strongly enhanced, unlike bands associated with cation vacancies. These results may be understood if mobile cation interstitials recombine with their vacancies [34].

In conclusion we would like to note, that there is so far no correct information on the optical properties of anion and cation interstitials, even in simple oxides as MgO and Al_2O_3, despite a lot of speculative suggestions. We illustrate this by a few examples. In 1980 Evans and Stapelbroeck [35] tentatively assigned the absorption band at 4.09 eV, formed under neutron irradiation or due to Al^+ implantation, to Al^+ interstitials. Later, Springis and Valbis [36] have exploited this idea as the model for the 4.1 eV absorption band in their studies of the relevant luminescence bands at 2.45 and 3.8 eV excited therein. However, in all *recent* experimental and theoretical papers the absorption band at 4.1 eV is already associated with dimer F_2 centres [3, 4, 37]. A second example is that a model for the 4.1 eV absorption band has been exploited to prove subthreshold defect creation in the corundum cation sublattice under 300 keV electron irradiation [38, 39], although at that time it was known already that the aluminium displacement threshold energy is only 175 keV [6].

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