Ab initio simulations on Frenkel pairs of radiation defects in corundum

A Platonenko, S Piskunov, Yu F Zhukovskii and E A Kotomin

Institute of Solid State Physics, University of Latvia, 8 Kengaraga Str, Riga, Latvia
E-mail: alexander.platonenko@gmail.com

Abstract. Large scale first principles periodic calculations based on the density functional theory within the localized atomic orbital approach (DFT-LCAO) using the hybrid exchange-correlation potential B3PW have been performed in order to study the structural and electronic properties of radiation-induced Frenkel pairs \( \text{O}^+\text{V} \) in corundum crystal. As an initial approach, we have used conventional \( 2 \times 2 \times 1 \) supercell for defective \( \alpha\text{-Al}_2\text{O}_3 \) lattice containing 120 atoms. After relaxation of the ideal supercell structure, the optimized \( d_{\text{O}^+\text{V}} \) distance has been found to be \( \sim 4.5 \) Å while the formation energy of Frenkel pair has achieved 11.7 eV. The interstitial \( \text{O}^+ \) atom, both single and a component of \( \text{O}^+\text{V} \) pair, spontaneously forms a dumbbell with the adjacent atom in the regular oxygen sublattice (\( d_{\text{O}^+\text{-O}} = 1.404 \) Å) with the induced charge \(-1.1\) e. On the whole, possibilities of supercell model for proper description of Frenkel pairs with changing inter-defect distance and space orientation inside corundum crystal are rather limited. This is why the alternative cluster model must be developed for this aim.

1. Introduction

Corundum (\( \alpha\text{-Al}_2\text{O}_3 \)) is important radiation-resistant material with potential applications for components of diagnostics, breeder blanket and in future fusion reactors as coating to avoid the light gases permeation, as well as corrosion produced by lithium-based alloys [1]. Induced changes in structural and optical properties of radiation-exposed \( \alpha\text{-Al}_2\text{O}_3 \) crystalline materials are mainly associated with oxygen vacancies \( \text{V}_\text{O} \) and complementary Frenkel pairs of defects (\( \text{O}_\text{V}+\text{V}_\text{O} \)) [2]. Despite technological importance of corundum crystalline structures, their fusion applications and prospects as a laser and dosimeter material, the point, e.g., electronic, defects have not yet comprehensively studied theoretically [2]. The main reasons for this are the following: the complicated atomic structure of \( \alpha\text{-Al}_2\text{O}_3 \) (Fig. 1) as well as the semi-covalent and semi-ionic chemical bonding as was experimentally observed using X-ray scattering [3]. Moreover, after formation of defect pair in perfect corundum crystal, a dramatic lowering of its initial symmetry \( R\bar{3}c \) (local space group \( D_{3d}^6 \)) occurs, thus, calculations of Frenkel pairs require significant computational time and resources.

Limited number of theoretical studies on point defects and Frenkel pairs in corundum is available, where empirical, semi-empirical and first-principle methods were used [2, 4-7]. While there is information about some mechanisms of defect formation, recombination and clustering, the reported formation energies of oxygen vacancy in corundum vary in a wide range from 4.9 to 13.3 eV [8-10]. Interpretation of experimental data also is still discussable theme [11].

In this study, we have consequently performed first principles calculations on (i) perfect corundum structure, (ii) that containing single point defects, such as neutral oxygen vacancy \( \text{V}_\text{O} \) and interstitial oxygen atom \( \text{O}_\text{i} \), (iii) that containing Frenkel pair \( \text{O}_\text{V}+\text{V}_\text{O} \), as well as (iv) that containing dumbbell \( \text{O}_\text{i}+\text{O}_{\text{reg}} \) pair in the case of \( \alpha\text{-Al}_2\text{O}_3 \) structures containing either single \( \text{O}_\text{i} \) impurity (as described earlier for defective \( \text{MgO} \) bulk [12]) or Frenkel pair. Using optimization procedure, we have determined...
equilibrium locations and configurations of \( V_0 \), \( O_i \), and \( O_i^+ \) inside corundum lattice. We have tested basis sets of Al and O atoms for adequate description of \( \alpha\)-\( Al_2O_3 \) properties: lattice and elastic constants as well as cohesion energies and band gaps, in order to choose the most appropriate model and computational details, \textit{e.g.}, exchange-correlation functional [13]. We also discuss limits for application of periodic supercell model for adequate description of radiation defects in corundum. The paper is organized as follows: details of calculations, \textit{e.g.}, atomistic models of defective \( \alpha\)-\( Al_2O_3 \) are discussed in Section 2, main results obtained for optimized Frenkel pairs in corundum are analyzed in Section 3, while main conclusions drawn in this study are summarized in Section 4.

2. Computational details

Large-scale \textit{ab initio} calculations have been performed combining the linear combination of atomic orbitals (LCAO) and hybrid exchange-correlation Becke-Perdew-Wang (B3PW) functional as implemented in \textit{CRYSTAL’14} computer code [13]. Such hybrid functional allows us to perform very accurate calculations of the band gap and other properties as compared to those obtained using other hybrid functionals (Table 1). The basis sets of Al and O have been selected and optimized in order to achieve reasonable compromise between the calculation accuracy and computational time. We have selected the corresponding basis sets with smaller number of Gaussian-type functions: (i) for aluminum, we have used the effective core pseudopotential (ECP) with 3\( s^2 3p^1 \) external shell as developed by Causá [14], (ii) while for oxygen, we have applied the full basis set in the form of 6\( s^2 2p^1 1d \) developed by Baima \textit{et al} [15]. For calculation on the formation energy of free oxygen molecule, this basis set has been extended by adding \( sp \)-function with diffuse exponents.

Table 1. Lattice parameters \( a \) and \( c \), band gap and formation enthalpy as well elastic constant for perfect corundum calculated using different hybrid and pure DFT exchange-correlation potentials.

| Method (functional) | \( a \), \( \Delta a^* \) | \( c \), \( \Delta c^* \) | Band gap, \( \Delta E_g^* \) | Formation enthalpy, \( \Delta E_{form}^* \) | Elastic constants, GPa [19] |
|---------------------|----------------|----------------|----------------|----------------|------------------|
| Experimental        | 4.76 [16]      | 12.99 [16]    | 8.8 [17]       | -17.36 [18]    | 496.5            |
| B3PW                | 4.775 0.32     | 12.979 -0.02  | 8.39 -4.7      | -19.45         | 12.0             |
| B3LYP               | 4.792 0.67     | 13.036 0.41   | 8.55 -2.8      | -20.19         | 16.3             |
| HSE-sol             | 4.744 -0.35    | 12.884 -0.75  | 8.25 -6.3      | -19.70         | 13.5             |
| PWGGA-HF25          | 4.761 0.02     | 12.944 -0.30  | 8.86 0.7       | -19.41         | 11.8             |
| PBE (DFT)           | 4.788 0.59     | 12.987 0.04   | 6.01 -31       | -18.69         | 7.7              |
| PWGGA (DFT)         | 4.816 1.18     | 13.072 0.70   | 6.31 -28.3     | -18.69         | 7.7              |

*as compared to experimentally found values written in previous columns;

** \( E_{form} = E_{tot}^{\text{AlO}_3(\text{perfect})} - 4E_{tot}^{\text{Al}} - 6E_{tot}^{\text{O}} \)

(1)
Figure 1. Images of Frenkel pair in initial and optimized corundum structures (left and right panels, respectively). \( V_O \) vacancy is shown as a black ball while interstitial \( O_i \) atom is shown as a blue (dark grey) one. Configurations of \( H \) center (or dumbbell) are shown as a dotted rectangle.

Formation energies for various defects in \( \alpha-\text{Al}_2\text{O}_3 \) have been calculated using following equations:

\[
E^\text{Oh}_{\text{form}} = E^\text{tot}_{\text{Oh}} - E^\text{Al}_2\text{O}_3(\text{perfect}) - E^\text{tot}_{\text{O}} \quad (2)
\]

\[
E^{\text{Vo}}_{\text{form}} = E^\text{tot}_{\text{Vo}} - E^\text{Al}_2\text{O}_3(\text{perfect}) + E^\text{tot}_{\text{O}} \quad (3)
\]

\[
E^\text{pair}_{\text{form}} = E^\text{tot}_{\text{pair}} - E^\text{Al}_2\text{O}_3(\text{perfect}) \quad (4)
\]

Within the SCF procedure, the accuracies (tolerances) \( 10^{-7}, 10^{-7}, 10^{-7}, 10^{-14} \) have been chosen for calculations of Coulomb and exchange integrals [13]. Effective charges on atoms have been estimated using Mulliken population analysis [20]. The integration over Brillouin zone in the reciprocal space has been performed with a 4x4x4 Pack-Monkhorst grid. When modeling the Frenkel pairs in corundum bulk, the 2x2x1 supercell model containing 120 atoms has been chosen (Fig. 1). All the calculations were performed with the total optimization of geometry. Obviously, the band gaps of perfect corundum, as presented in the upper part of Table 1 obtained using various hybrid DFT+HF methods, are much closer to the experimental value than those obtained within pure DFT method.

3. Results and analysis

Firstly, we have performed first principles calculations on single oxygen neutral point defects. Interstitial \( O_i \) atom initially introduced to the octahedral center between the two nearest oxygen triangles across \( \alpha-\text{Al}_2\text{O}_3(0001) \) plane (left panel of Fig. 1) has been displaced towards one of the apexes shown by dashed rectangle after energy optimization, with energy gain of 3.84 eV (qualitatively analogously to displacement of \( O_i \) apexes shown by dashed rectangle after energy optimization, with energy gain of 3.84 eV (qualitatively analogously to displacement of \( O_i \) atom from the cube-centered position in \( \text{MgO} \) unit cell estimated earlier [12]). Initial configuration of vacancy \( V_O \) has been chosen by such a way, to provide its location between the central oxygen planes of corundum supercell. Vacancy was created by fully removing \( O \) atom from crystal structure. As a result of geometry optimization, \( V_O \) point defect has been displaced from its initial position too. Influence of both defects on the nearest neighbor atoms is shown in Table 2 (note that the two of four \( \text{Al} \) neighbors are located closer to the oxygen vacancy than the other two, the same is true for oxygen neighbors).

### Table 2. Structural relaxation of the lattice area around arbitrary neutral defect in the Frenkel pair (Fig. 1). For arbitrary defect, its distances (in Å) to 1NN-4NN atoms in the perfect crystal (located at the nearest and next-nearest neighboring atomic spheres) are shown first, followed by the changed distances (\( \Delta d \)) and changes of induced charges (\( \Delta q_{\text{Al}} \) or \( \Delta q_{\text{O}} \)) after the geometry optimization.

| Type of site or defect | 1NN | \( \Delta d \)% | \( \Delta q_{\text{Al}} \) | 2NN | \( \Delta d \)% | \( \Delta q_{\text{Al}} \) | 3NN | \( \Delta d \)% | \( \Delta q_{\text{Al}} \) | 4NN | \( \Delta d \)% | \( \Delta q_{\text{Al}} \) |
|-----------------------|-----|---------------|----------------|-----|---------------|----------------|-----|---------------|----------------|-----|---------------|----------------|
| Interstitial site*    | 1.92 (2 Al) - | -2.6 | 0.0 | 1.98 (6 O) | 1.0 | 8.59 | 0.00 | 2.82 | 2.17 | -0.02 | 3.3 | 1.02 | 0.00 |
| Interstitial \( O_i \) atom** | 1.87 | -2.6 | 0.0 | 2.15 | 2.52 | 5.95 | +0.07 | 2.82 | 2.17 | -0.02 | 3.3 | 1.02 | 0.00 |
| Regular \( O \) site* | 1.86 (2+2 Al) | 1.97 | 0.2 | 2.52 | 2.62 | 5.24 | (2+2 O) | 2.72 | 2.87 | (4+4 O) | 3.22 | 3.43 | (3+3 Al) |
| \( V_O \) vacancy | 1.77 | -4.84 | -0.37 | 2.50 | -0.79 | +0.02 | 2.72 | 0.00 | +0.02 | 3.23 | 3.42 | 1.0 | 1.0 |

*brackets in rows contain numbers and chemical symbols of the nearest atoms as follows from Fig. 1a; **results for \( O_i \) impurity atom are obtained for its location at the center of oxygen octahedron

Formation energies of single point defects are 4.21 eV for interstitial oxygen atom defined by Eq. (2), possessing induced charge \(-0.5 \text{ eV} \), as well as 7.60 eV for oxygen vacancy defined by Eq.(3)
respectively. Since there is noticeable change in charges of Al atoms (-1.2 $e$ in total for 4 Al atoms) of 1NN sphere of the vacancy we can assume that it is positively charged. Sum of both defect formation energies is 11.81 eV, what is reasonable for formation of well separated (>15 Å) Frenkel pair.

In perfect corundum crystal, the effective atomic charges have been found to be -1.0 $e$ for O and 1.5 $e$ for Al atoms, respectively, while considerable contribution of the covalency to the chemical bonding have been found to be too: 0.386 $e$ and 0.262 $e$ (for smallest values of $d_{\text{Al-O}}$ equal to 1.858 Å and 1.968 Å, respectively). The Frenkel pair has been modeled inside the conventional 2×2×1 supercell with 4.42 Å distance between $V_O$ vacancy and O atom. Interstitial O atom also forms a dumbbell with adjacent regular O atom after energy optimization ($d_{\text{Oi-Oj}} =$ 1.404 Å) with total charge $-1.1\, e$. Mulliken population analysis shows that the bond population between Al atom and dumbbell oxygen atoms is almost twice smaller than that in regular Al–O bond (0.198 $e$ vs. 0.386 $e$, respectively). After geometry relaxation $\text{O}_i-\text{V}_O$ distance has been found to be ~4.4 Å. Al atoms inside the first coordination sphere around $V_O$ vacancy possess smaller charges (1.12–1.27 $e$) as compared to that in perfect corundum (1.5 $e$), so it seems that vacancy tends to be slightly positively charged. In the next coordination spheres, induced charges towards $V_O$ vacancy has been found to be almost neglecting. The formation energy of Frenkel pair in α-Al$_2$O$_3$ has been obtained to be 11.7 eV. It is close to sum of formation energies for single O$_i$ and $V_O$ defects obtained separately as mentioned above 11.81 eV (4.21 eV + 7.60 eV). Values of $E_{\text{pair}}^{\text{form}}$ found earlier were reported in a range 4.87–8.27 eV [10], whereas in other theoretical studies, this value achieved 13.3 eV [8,9]. Still, our result may be overestimated because of defect-defect interactions in supercell model.

For further calculations, we are going to use conventional supercell of 3×3×1 extension, where initial length of the Frenkel pair can be chosen as a more realistic value (7.0–7.2 Å), as also to compare results and evaluate defect-defect interaction in periodic model. As to further increase of the conventional supercell for simulation of Frenkel pairs, $d_{\text{Oi-Vj}}$, distance in which can achieve 15–17 Å (as observed in experiments), it cannot be realized in principle. This is why, in order to provide further possibility to simulate a series of Frenkel pairs in corundum with consequently increasing $d_{\text{Oi-Vj}}$ length, we plan to perform large-scale cluster model calculations using the NWChem code [21]. Moreover, the first-principles formalism realized in this code foresee the possibility to consider not only neutral defects as in periodic calculations but also charged and excited defects.

4. Conclusions

First-principle periodic calculations have been performed in order to study the structure and formation energies of point and pair-wise defects in corundum. It has been found that the interstitial oxygen atom in both absence and presence of $V_O$ in α-Al$_2$O$_3$ can form dumbbell $H$-centers like in MgO bulk [12]. Behavior of oxygen vacancy is similar in both cases: it tends to be positively charged.

In order to simulate well-separated Frenkel pairs of varying length as well as charged and excited defects, a cluster model will be used in the next studies, which also excludes artifacts caused by the periodic network of defect-defect interactions.

Acknowledgements

This work has been carried out within the framework of the EUROfusion Consortium and has received funding from the European Union’s Horizon 2020 research and innovation programme under grant agreement number 633053. The authors thank also Latvian LZP grant No.237/2012 for financial support. The views and opinions expressed herein do not necessarily reflect those of the European Commission. Authors thank R Vila and A I Popov for fruitful discussions.

References

[1] F.Mota, C.J.Ortiz, R. Vila, N. Casal, A. Garcia, A. Ibarra. 2013 J Nucl Mater 442 5699
[2] Jacobs P W M and Kotomin E A 1994 J Amer Ceram Soc 77 2505
[3] Lewis J, Schwarzenbach D, and Flack H D 1982 Acta Crystallogr A 38 733
[4] Zhukovskii Yu F, Sokol A A, Kotomin E A, Catlow C R A, and Nieminen R M 1997 J Phys Cond Matt 9 3559
[5] Kotomin E A, Popov A I, and Stashans A 1998 Phys Status Solidi B 207 69
[6] Catlow C R A, James R, Mackrodt W C, and Stewart R F 1982 Phys Rev B 25, 1006
[7] Grimes R W, 1994 J Amer Ceram Soc 77 378
[8] Hine N D M, Frensch K, Foulkes W M C, and Finnis M W 2009 Phys Rev B 79 24122
[9] Janetzko F, Evarestov R A, Bredow T, and Jug K 2004 Phys Status Solidi B 241 1032
[10] Matsunaga K, Tanaka T, Yamamoto T, and Ikuhara Y 2003 Phys Rev B 68 085110
[11] Evans B D 1995 J Nucl Mater 219 202
[12] Brudevoll T, Kotomin E A, and Christensen N E 1996 Phys Rev B 53 7731
[13] Dovesi R, Saunders V R, Roetti C, Orlando R, Zicovich-Wilson C M, Pascale F, Civalleri B, Doll K, Harrison N M, Bush I J, D’Arco Ph, Llunell M, Causá M, and Noël Y 2014 CRYSTAL14 User’s Manual (University of Torino)
[14] Causá M, Dovesi R, and Roetti C 1991 Phys Rev B 43 11937
[15] Baima J, Erba A, Rerat M, Orlando R, and Dovesi R 2013 J Phys Chem C 117 12864
[16] Lutterotti L and Scardi P 1990 J. Appl. Crystallogr 23 246
[17] French R H 1990 J. Am. Ceram. Soc. 13 471
[18] Zumdahl S S 2009 Chemical Principles (6th Edition, Houghton Mifflin Co, Boston, New York)
[19] Gladden J R, Maynard J D, So J H, Saxe P, and Le Page Y 2004 Appl Phys Lett 85 392
[20] Mulliken R S 1955 J Chem Phys 23 1833
[21] Valiev M, Bylaska E J, Govind N, Kowalski K, Straatsma T P, Van Dam H J J, Wang D, Nieplocha J, Apra E, Windus T L, and De Jong W A 2010 Comput Phys Commun 181 1477