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Molecular dynamics study of high-pressure alumina polymorphs with a tight-binding variable-charge model

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ABSTRACT

A tight-binding variable-charge model aimed at performing large-scale realistic simulations of bulk, surfaces and interfaces of aluminum oxides have been developed. This model is based on the charge equilibration (QEq) method and explicitly takes into account the mixed iono–covalent character of the metal–oxygen bond by means of a tight-binding analytical approach in the second-moment approximation of the electronic structure. The parameters of the model were optimized to reproduce structural and energetic properties of the α-Al_2O_3 corundum structure at room temperature and pressure. The model exhibits a good transferability between five alumina polymorphs: corundum, Rh_2O_3(II)-type, perovskite (Pbnm), $CaIrO_3$-type and U_2S_3-type structures. In this paper, we present results obtained by molecular dynamics for pressure ranging from 0 to 500 GPa. First, static relaxations reproduce satisfactorily experimental and *ab initio* results concerning the stability domains and transitions from corundum to Rh_2O_3(II) and then to $CaIrO_3$-type structure when pressure increases. At higher pressure, the transition from $CaIrO_3$ to U_2S_3 structure is also observed at a pressure significantly lower than that given *ab initio*. Molecular dynamics confirm these results and also predict a phase transition at about 400 GPa from corundum to a triclinic structure.

1. Introduction

Alumina has important applications in high-pressure science, geophysics and ceramic science. Single-crystal Al_2O_3 (sapphire) is often used in shock wave experiments as a high-pressure optical window or as a high-pressure electrical insulator. When doped with Cr^{3+} (ruby) it is used as pressure calibrant in diamond-anvil-cell experiments. Alumina is also an important mineral component in earth's mantle. Phase transitions in alumina under pressure have been extensively studied by experimental and theoretical approaches [1–8]. All these studies agree to predict first a phase transition from corundum to Rh_2O_3(II)-type structure around 80 GPa and then to $CaIrO_3$-type post-perovskite phase after 130 GPa [2]. Moreover, a transition at 370 GPa is theoretically predicted from $CaIrO_3$ to U_2S_3-type structure [3].

Ab initio approaches can predict the stability range for the different structures as a function of the applied pressure but the study of the kinetics of transitions is more difficult due to the small size of the systems which can be handled. On the other hand, molecular dynamics based on empirical potentials allows such studies with a reasonable accuracy leading to a better understanding of the mechanisms at the atomic scale. Ten years ago, Jahn et al. [9] used an anisotropic-ion model (AIM) developed previously [10,11] to perform dynamic simulations of pressure-driven phase transformations in Al_2O_3. The parameters of the AIM model were obtained from *ab initio* calculations performed on different crystal structures and the liquid state, ensuring the transferability of the potential. This fitting procedure is rather accurate but is extremely cumbersome and very computer time consuming. In this paper, we propose to study the high-pressure behavior of alumina at the atomic scale by using a recent semi-empirical variable-charge model based on a tight-binding approach in the second-moment approximation. The so-called SMTB-Q model (Second-Moment Tight-Binding-QEq) aimed at described iono–covalent compounds (bulk, surface, defects) [12–15] depends on a limited number of parameters adjusted on the physical properties of only one phase, here α-Al_2O_3 at ordinary temperature and pressure. The properties of the other phases are obtained without additional fitting. Moreover, the second-moment framework supplies an analytical expression for both ionic charges and covalent energy of the compound, which ensures fast calculations.

This article is organized as follows. A first part is dedicated to the description of the SMTB-Q model and to the optimization of

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its intrinsic parameters as well as to the properties of bulk α-Al_2O_3 and their (0001) and (1 −102) surfaces. In a second part, the results obtained in static conditions for the different structures, from 0 to 500 GPa are presented, following by those obtained by molecular dynamics. The last part is devoted to our conclusions.

2. Computational methods

2.1. The SMTB-Q model

The variable-charge scheme of the SMTB-Q model is based on the QEq formalism proposed by Rappé and Goddard [16] and allows the ionic charges to vary according to their local environment. Let us note that several variable-charge models based on this formalism have been previously developed for oxides, among which those of Ogata et al. [17] and Streitz and Mintmire [18]. On the other hand, the SMTB-Q model exploits the quantum description of insulating oxides proposed by Goniakovski and Noguera [19,20]. Thus, the cohesive energy, E_{coh}, of a simple binary oxide M_nO_m is the sum of four terms: ionic, coulombic, covalent and repulsive:

$$E_{coh} = E_{ion} + E_{coul} + E_{cov} + E_{rep}, \tag{1}$$

with:

$$E_{ion} = \sum \left(E_A^0 + \chi_A^0 Q_A + 1/2 J_{AA}^0 Q_A^2 \right), \tag{2}$$

$$E_{coul} = \sum_{A} \sum_{B<A} Q_A Q_B J_{AB}, \tag{3}$$

$$E_{cov} = - \sum_{i(i=\mathrm{M,O})} \left\{ \sum_{\substack{j(j=\mathrm{O,M}) \\ r_{ij} \leqslant r_C}} \beta_i^2 \exp\left[-2q \left(\frac{r_{ij}}{r_{\mathrm{OM}}^0} - 1 \right) \right] \Delta Q_i \right\}^{1/2}, \tag{4}$$

$$\begin{aligned} E_{rep} = & \sum_{i(i=\mathrm{M,O})} \sum_{\substack{j(j=\mathrm{O,M}) \\ r_{\mathrm{OM}} \leq r_C}} A_\mathrm{M} \exp\left[-p_\mathrm{M} \left(\frac{r_{ij}}{r_{\mathrm{OM}}^0} - 1 \right) \right], \\ & (\text{metal—oxygen pairs}) \\ & + \tfrac{1}{2} \sum_{\mathrm{O}} \sum_{\mathrm{O}, r_{\mathrm{OO}} \leq r_C} B \exp\left(\tfrac{r_{\mathrm{OO}}}{\rho}\right). \quad (\text{oxygen—oxygen pairs}) \end{aligned} \tag{5}$$

E_{ion} (Eq. (2)) is the ionization energy developed up to the second order with respect to the charges Q_A on atom A, E_A^0 is the energy of the neutral atom and χ_A^0 and J_{AA}^0 are the electronegativity and the hardness of the atom A respectively. E_{coul} (Eq. (3)) is the electrostatic energy with J_{AB} the coulomb interaction between the charges on centers A and B. Following Rappé and Goddard [16], J_{AB} are coulomb integrals between two single s-type Slater orbitals $\rho_A(r) = N_n r^{n-1} e^{-(2n+1)/4R_A}$, where N_n is the normalization constant, n is the quantum number of outer valence orbital and R_A is the covalent radius of atom A in the original QEq formulation [16]. In a solid, the real significance of R_A is more complex because it depends both on the coordination number of the atom and on the interatomic distance which forces us to consider it as an adjustable parameter. At short distance, the coulomb interaction is shielded, leading to a decrease on the absolute value of the electrostatic energy compared with the one obtained with point-charge models [21]. The covalent energy, E_{cov} (Eq. (4)), is derived from the quantum model developed by Noguera and Goniakovski [19,20] and is detailed in a recent article [13]. The covalent interaction is extending over all neighbors of every atom (M or O) up to the second-moment cut-off radius r_c located between the 4th and 5th neighbors [22]. r_{OM}^0 is the equilibrium first-neighbor O–M distance, β_i (the hopping integral) and q are adjustable parameters. β_i is different if atom i is a metal or an oxygen given the relationship $\beta_\mathrm{O}^2 Z_\mathrm{O} = \beta_\mathrm{M}^2 Z_\mathrm{M}$ derived in Appendix A in [13], where Z_O and Z_M are the coordination number of oxygen and metal respectively. ΔQ_i is the part of covalent interaction which depends on the charge delocalization $\delta q_i = \left| Q_i^F \right| - |Q_i|$ (Q_i^F and Q_i are the formal and the real charge of atom i respectively) by the relation:

$$\Delta Q_i = \delta Q_i (n_{cov}^i - \delta Q_i), \tag{6}$$

where n_{cov}^i is the number of orbitals of an ion hybridazed with the orbitals of its neighboring ions of opposite nature. Let d_M and d_O the numbers (or degeneracies) of outer orbitals of the metal and oxygen in an oxide M_nO_m. The number of hybridized orbitals is then:

$$n_0 = \min(n d_\mathrm{M}, m d_\mathrm{O}). \tag{7}$$

Thus each oxygen shared $n_{cov}^\mathrm{O} = n_0/m$ orbitals with their metallic neighbors and each metal shared $n_{cov}^\mathrm{M} = n_0/n$ orbitals with their oxygen neighbors.

Eq. (5) represents the short-range pair repulsion between ions. A_M, p_M, B and ρ are adjustable parameters. Cation–cation short-range interactions are neglected because the M outer orbitals are empty in an insulator.

The equilibrium distribution of charges is obtained according to the equalization of either the electronegativities (χ_i) or the electronic chemical potentials (ECP) (μ_i), these two quantities being of opposite sign ($\chi_i = -\mu_i$). In this work, the equilibrium charges are calculated by using the dynamical fluctuating charge model [23] that equalizes the ECP of each ion with the average ECP in the oxide:

$$\forall i \quad \mu_i = \frac{\partial E_{tot}}{\partial n_i^e} = \overline{\mu}, \tag{8}$$

where n_i^e is the number of electrons on an ion i. μ_i may be separated into an electrostatic part and a covalent part:

$$\mu_i = \mu_i^{ES} + \mu_i^{cov}. \tag{9}$$

From Eqs. (8) and (9), we obtain the charge delocalization on an oxygen:

$$\delta Q_i = n_{cov}^i \left(1 - \frac{\left| \mu_i^{ES} - \overline{\mu} \right|}{\sqrt{\left(\mu_i^{ES} - \overline{\mu} \right) + 4 Z_i \beta_i^2}} \right). \tag{10}$$

In a homogeneous M_nO_m bulk, $\mu_\mathrm{O}^{cov} = -\mu_\mathrm{M}^{cov}$ and it follows that: $\overline{\mu} = (\mu_\mathrm{M}^{ES} + \mu_\mathrm{O}^{ES})/2$. Then, the expression (10) rewrites:

$$\delta Q_i = n_{cov}^i \left(1 - \frac{\left| \mu_i^{ES} - \overline{\mu} \right|}{\sqrt{\left(\mu_\mathrm{M}^{ES} - \mu_\mathrm{O}^{ES} \right)^2 + 4 Z_i \beta_i^2}} \right). \tag{11}$$

Comparing this expression with that obtained by Noguera et al. [19,20] in the framework of the second-moment approximation of the tight-binding scheme:

$$\delta Q_i = n_{cov}^i \left(1 - \frac{\varepsilon_\mathrm{M} - \varepsilon_\mathrm{O}}{\sqrt{\left(\varepsilon_\mathrm{M} - \varepsilon_\mathrm{O} \right)^2 + 4 Z_i \beta_i^2}} \right), \tag{12}$$

where ε_M and ε_O are the energy of the atomic orbitals of metal and oxygen respectively. It follows that μ_M^{ES} and μ_O^{ES} are equivalent to ε_M and ε_O respectively.