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Molecular-dynamics simulation of threshold displacement energies in zircon

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ABSTRACT

Molecular-dynamics simulations were used to examine the displacement threshold energy (E_d) surface for Zr, Si and O in zircon using two different interatomic potentials. For each sublattice, the simulation was repeated from different initial conditions to estimate the uncertainty in the calculated value of E_d. The displacement threshold energies vary considerably with crystallographic direction and sublattice. Based on the present simulations and previous experimental studies, this work recommends E_d values of 75, 75 and 60 eV for Zr, Si and O, respectively, to be used in Monte Carlo simulations of irradiation damage profile in zircon.

1. Introduction

Zircon ($ZrSiO_4$) is a candidate host material for the disposition of nuclear waste and the immobilization of excess weapons plutonium [1,2]. Zircon occurs in nature with U and Th concentrations typically around 5000 ppm and as high as 10 wt.% [1]. It is an important mineral for U–Pb radiometric dating to determine the age of fossils. During α-decay, the crystalline lattice of $ZrSiO_4$ is heavily damaged, and atoms are displaced from their lattice sites. The transformation of zircon to the metamict (disordered) state due to radiation damage is well known [3,4]. Accumulated radiation damage can be detrimental to the mechanical integrity of zircon. It can lead to undesirable leaching of actinides in wasteform applications and can contribute to accelerated Pb and U loss in natural zircon, which has important implications for geochronology. Therefore, it is essential to understand defect production and displacement damage in irradiated zircon. A key parameter in studies of radiation damage is the displacement threshold energy (E_d), which is the minimum energy to produce a stable defect on a particular sublattice. Due to the small time and length scales of the radiation damage production process and the difficulty in associating experimentally observed damage uniquely to a specific sublattice, atomistic simulations are needed to shed light on the displacement process.

In molecular-dynamics (MD) simulations of radiation damage, a Primary Knock-on Atom (PKA) is given velocity in a specific direction corresponding to the initial kinetic energy of a recoil atom and the evolution of all the atoms is followed based on an empirical interaction potential. Previously, we had determined E_d for Zr, Si and O in zircon [5] to be about 90, 20 and 53 eV, respectively, based on static calculations performed for only one or two directions for each sublattice. Static calculations may not accurately capture the dynamics of energetic recoil damage. A previous MD study [6] of displacement energies in zircon with a formal charge model reported E_d for Zr, Si and O as 98, 48 and 23 eV, respectively. However, this study used an interatomic potential that does not reproduce the lattice constants well and suffers from shear instability.

Previously, we have employed a partial charge model [7] to perform extensive atomistic simulation studies of displacement damage produced by high-energy recoils in zircon [8]. However, this model cannot correctly model the phase separation of zircon into ZrO_2 and SiO_2, which is known to occur under certain irradiation conditions [9]. ZrO_2 and SiO_2 are not neutral entities in the above model [7] based on the assignment of partial charges of +3.8 for Zr, +2 for Si and −1.45 for O. Since the reliability of MD is determined by the fidelity of the potential, a reliable potential is needed

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to simulate the production of radiation damage in $ZrSiO_4$, correctly model phase separation of $ZrSiO_4$ into ZrO_2- and SiO_2-rich regions, and model ZrO_2–SiO_2 interfaces. Recently, we have developed such a potential and demonstrated that it is well-suited to study the structure and mechanical properties of various phases of $ZrSiO_4$, ZrO_2 and SiO_2 [10]. This potential assigns partial charges of 2.4, 2.4 and −1.2 to Zr, Si and O, respectively. In the present report, the former potential [7] will be referred to as the unequal-charge potential and the latter [10] as the equal-charge potential based on the equality of Zr and Si partial charges.

The use of a fixed charge model imposes serious limits on the transferability of the potential. From the standpoint of electronegativity, it is intuitive that the partial charge of Zr must be greater than that of Si as in our earlier potential [7]. It can be argued that by choosing a potential that permits phase decomposition, one reduces the accuracy of description of perfectly crystalline zircon while allowing for the possibility of phase separation. In fact, since displacement energy simulations involve sparse defect production in a perfect crystal, it is likely that the unequal-charge potential [7] may give more accurate displacement energies than the equal-charge potential [10]. Given the fact that there is no clear choice between the two models, the present work calculates displacement threshold energies along several crystallographic directions for the three sub-lattices in zircon obtained using these two potentials. The aim is to determine E_d in zircon and study how the number and types of defects obtained in previous simulations of radiation damage in zircon using the unequal-charge model would be modified by the use of the equal-charge model.

2. Simulation details

The unit cell of zircon is illustrated in Fig. 1. The crystal structure is body-centered tetragonal (space group $I4_1/amd$) with four $ZrSiO_4$ formula units per unit cell [11]. The arrangement of O is such that the structure consists of edge-sharing SiO_4 tetrahedra and ZrO_8 dodecahedra. Each Si is coordinated by 4 O at a bond distance of 1.62 Å, while each Zr is coordinated by 4 O at 2.13 Å and 4 O at 2.27 Å. Each O is bonded to two Zr and one Si, and there is no Si–O–Si polymerization in perfect crystal $ZrSiO_4$.

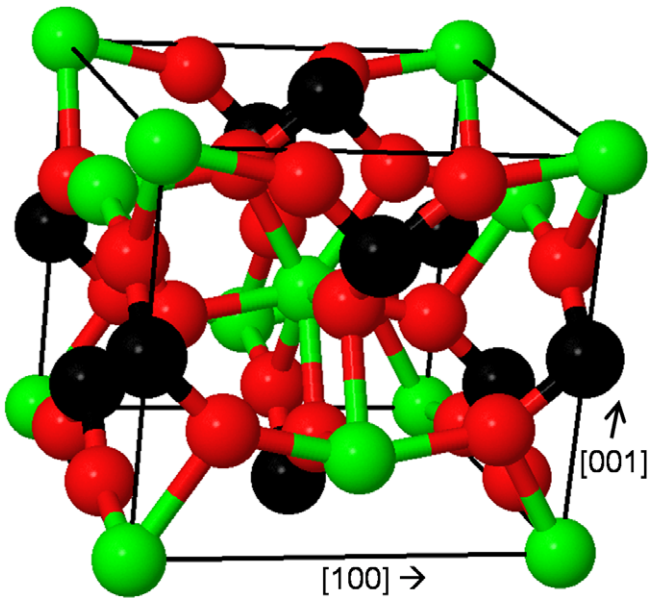

Fig. 1. The unit cell of zircon. Zr, Si and O are shown as green (light gray), black and red (dark gray) spheres, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Starting from this perfect crystal structure, MD simulations were performed using the DL_POLY code [12] developed at Daresbury Laboratory, UK. The simulation cell contained 3000 ions ($5 \times 5 \times 5$ unit cells). Periodic boundary conditions were used and the simulation cell was initially equilibrated at 300 K and zero external pressure with Berendsen's constant pressure and temperature ensemble [13] for 5 ps. The partial charge interatomic potentials used [7,10] were based on rigid-ion models and consist of a Coulomb term, a short-range Buckingham potential, and a repulsive term for close interatomic separations. The fitting procedure, and the use of a repulsive potential at close separations have been discussed in detail elsewhere [7,10]. The potentials are of the Buckingham potential form:

$$\phi(r_{ij}) = q_i q_j / r_{ij} + A_{ij} \exp\left(-r_{ij}/\rho_{ij}\right) - \frac{C_{ij}}{r_{ij}^6}. \quad (1)$$

Here, q_i and q_j are the charges of atoms i and j, r_{ij} is the interatomic distance, and A_{ij}, ρ_{ij} and C_{ij} are adjustable parameters. The potential parameters are listed in Table 1.

Table 2 presents a summary of the properties of perfect crystal zircon, such as lattice constants (a and c), elastic constants and dielectric constants obtained from the two potentials used here [7,10], the model of Park et al. [6] and experiment [14–20]. It is interesting to note that evaluating potentials based on fit to the density and bulk modulus can be misleading. The potential of Park et al. [6] matches the experimental value of density very well and provides a reasonable match to the experimental bulk modulus, but the individual lattice constants are poorly matched with the errors cancelling each other, and one of the elastic constants is negative. In fact, a is smaller than c according to this potential, while it is known from experiment that a is larger than c by about 10%. The best overall fit to the perfect crystal properties, including the static dielectric constant, is provided by the unequal-charge model [7].

The Zr, Si or O PKA was initiated from the equilibrated configuration, and the evolution of the system was simulated with the constant NVE ensemble for about 4 ps. The initial temperature was 300 K, and the temperature rise due to the PKA was in the range from 30 to 200 K. A variable time step algorithm was used to dynamically decrease the time step below 1 fs during the initial stages of the recoil when several ions have kinetic energy in excess of 1 eV. The kinetic energy imparted was increased in successive runs in steps of 32 eV from a starting value of 32 eV. If a displacement was produced at energy E_2 but not at a lower energy E_1, the next run was performed at $0.5(E_1 + E_2)$ and the procedure repeated until the difference between E_1 and E_2 was 1 eV. The occurrence of permanent displacement was determined based on the occupation of Voronoi polyhedra centered on lattice sites instead of counting the number of ions displaced by a certain distance, because the latter criterion can erroneously count replacements as displacements.

Table 1
Parameters of the two potential models used in the present work. The models are named after the charge of the Zr and Si cations.

Parameter	Equal charge [10]	Unequal charge [7]
q_{Zr} (e)	2.4	3.8
q_{Si} (e)	2.4	2.0
q_O (e)	−1.2	−1.45
A_{Zr-O} (eV)	17243.394	1967.0
ρ_{Zr-O} (Å)	0.2265	0.305004
C_{Zr-O} (eV/Å^6)	128.3513	0.0
A_{Si-O} (eV)	18003.7572	1277.0
ρ_{Si-O} (Å)	0.2052	0.227225
C_{Si-O} (eV/Å6)	133.5381	0.0
A_{O-O} (eV)	1388.773	1755.0
ρ_{O-O} (Å)	0.3623	0.30682
C_{O-O} (eV/Å^6)	175.0	0.0