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Structures and energetics of point defects with charge states in zircon: A first-principles study

Xiao-Yong Yang [a, b], Shuao Wang [c], Yong Lu [d], Peng Bi [a], Ping Zhang [b], Shahid Hussain [e], Yong Yi [a], Tao Duan [a, *]

[a] School of National Defense Science and Technology, State Key Laboratory for Environment Friendly Energy Materials, Southwest University of Science and Technology, Mianyang 621010, China
[b] Institute of Applied Physics and Computational Mathematics, Beijing 100088, China
[c] School for Radiological and Interdisciplinary Sciences and Collaborative Innovation Center of Radiation Medicine, Soochow University, Suzhou 215123, China
[d] College of Science, Beijing University of Chemical Technology, Beijing 100029, China
[e] School of Materials Science and Engineering, Jiangsu University, Zhenjiang 212013, China

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ABSTRACT

The fundamental problem of point defects under different phase equilibrium conditions in zircon ($ZrSiO_4$) is carried out by first-principles calculation. The formation energies with the structural deformation of various native defects, i.e., single vacancy, interstitial, Frenkel and Schottky pairs at different charge states are calculated, which agree well with the available results. We identify V_O^{2+} shows an important role in non-stoichiometric regime of $ZrSiO_{4-x}$ ($x < 1$). When Fermi level (ε_F) locates close to the CBM, the V_{Zr}^{4-} becomes more easily observed than V_O^{2+} in O-rich environment. In turn, the most abundant interstitial defects are I_{Zr}^{4+} and I_{Si}^{4+}. The non-interacting Si Frenkel-pair, made of the association of quadruply charged defect in energy of 5.947 eV, is more likely to form than other type of Frenkel-pairs. By formation the complex defects associating partial and full Schottky defects requires higher formation energy. These results provide a good reference to understand storage state as well as disposal of excess weapons-grade Pu and high-actinide wastes.

1. Introduction

The silicate mineral zircon ($ZrSiO_4$), a ubiquitous accessory mineral, possesses high dielectric permittivity, wide bandgap, and large energy band offset, which make it to be used as a high-κ gate dielectric material in metaloxide-semiconductor (CMOS) devices [1–5]. On the other hand, zircon has low thermal expansion coefficient, low thermal conductivity, high resistance to thermal shock, and exceptional low oxygen permeation rate, hence it is an important candidate for high-temperature structural material and anti-oxidation protective coating [6–9]. Particularly, due to its durability and ability to host large quantities of long-lived actinides into its crystal lattices, zircon is being considered as a ceramic host material to immobilize and dispose weapons-grade nuclear waste [10–13]. Thus, zircon has been attracted vast attentions from various scientists for many decades [8–14].

Up to now, large physical and chemical properties of zircon have been investigated in great detail from both theory and experiment [15–17]. For example, the phase transition from zircon (space group $I4_1/amd$) to scheelite structure (space group $I4_1/a$) has been studied in static high pressure and shock experiments at different value of pressure and temperature [18,19]. The diffusion rates of three tetravalent cations (U, Th, Hf) and three rare-earth elements (Sm, Dy, Yb) have been measured in synthetic zircon [12,13]. In theory, band structure, density of state, electron localization function and Bader charges are discussed for several possible structures of zircon by high throughput hybrid evolutionary algorithms together with first-principle calculations [20,21]. The $Pu^{3+} - Pu^{4+}$ electronic transition of Pu-doped zircon is evaluated based on density functional theory (DFT) [22,23]. Structural, electronic, and magnetic properties of the Fe-doped zircon mineral has been studied [24,25]. The activation energies and diffusion coefficients versus temperature for U and Pu in zircon are calculated respectively based on the transition state theory [26–28].

* Corresponding author.
E-mail address: duant@swust.edu.cn (T. Duan).

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In spite of the fact that zircon is one of the hardest silicates, it often contains several defects or impurities like any other material which would influence its final properties. To the best of our knowledge, the decay series of nuclides like in the ^{238}U, ^{235}U, and ^{232}Th in zircon lattices can lead to the structural damage and metamict state, mainly caused by α-decay irradiation. Earlier, Yada et al. observed many contrast anomalies of bright and dark spots in zircon lattice image which were demonstrated as point defects of vacancy and interstitial, produced by direct atomic collision with α-particles or by passage of ionizing nuclear particles [29]. However, the fundamental question about the formation mechanism of defects in energy under radiation effects has never been addressed, which is critical for actinides-doped with the diffusion property, designing or tailoring waste isolation hosts to minimize the release of actinides to the environment. In particular, the formation energies of various defects are the key input parameters for many higher scale simulation, including atomic Monte-Carlo, object/event based Monte-Carlo. Thus, the aim of the present work is to ascertain the energetics of intrinsic point defects with different charge states in $ZrSiO_4$ by first-principles calculation based on DFT. The rest of the paper is organized as follows. The first-principles computational method is briefly introduced in Sec. 2. Section 3 is devoted to determine and discuss the formation energies and structure deformation of all kinds of point defects in various charge states. Finally, a summary of the study is given.

2. Computational method

The DFT calculations are performed using the projector-augmented-wave (PAW) method [30] with the local density approximation (LDA) and the generalized gradient approximation (GGA) [31,32] for the exchange-correlation energy, as implemented in the Vienna *ab initio* simulations package (VASP) [33]. Twelve electrons ($4s^2 4p^6 4d^2 5s^2$) for zirconium (Zr), four electrons ($3s^2 3p^2$) for silicon (Si), and six electrons ($2s^2 2p^4$) for oxygen (O) are taken into account as valence electrons. A $2 \times 2 \times 1$ supercell (containing 96 atoms) has been employed to model the defects formation in $ZrSiO_4$. For the 96-atom supercell calculations, a $5 \times 5 \times 5$ *k*-point mesh is used in Brillouin zone (BZ) integrations [34]. Our test calculations show that such a *k*-point mesh could guarantee an energy convergence of 0.1 meV per atom. The electron wave functions are expanded in plane waves up to a cutoff energy of 600 eV, which is sufficient for errors in the formation energy of different defects less than 1 meV. During the calculation of the total energy of defective structure, the shape and size of the supercell are fixed while the fractional atomic coordinates are relaxed until the Hellmann-Feynman forces are less than 0.01 eV/Å. Spin polarization is included in all the energy calculations.

$ZrSiO_4$ is a promising candidate to immobilize weapons-grade nuclear waste and other minor actinides, which contain di-, tri-, tetra-, and hexa-valent actinides, such as Sm^{2+}, Eu^{2+}, Pu^{3+}, Nd^{3+}, Gd^{3+}, Pu^{4+}, U^{4+}, Pr^{4+} and so on [12,13]. In addition, $ZrSiO_4$ and the released nuclides might interact with underground water flow which contains H^+ and OH^-. All these impurities may provide effective charges for point defect. Thus six kinds of point defects are considered: Zr vacancy (V_{Zr}), Zr interstitial (I_{Zr}), Si vacancy (V_{Si}), Si interstitial (I_{Si}), O vacancy (V_O), and O interstitial (I_O). The charge states from −4 to +4 and from −2 to +2 are considered for Zr-related (or Si-related) defects and O-related defects, respectively. The additional charges are modeled by adding or removing electrons from the supercell. From the total energies calculated for the defect-free and defect-containing boxes, one can obtain the formation energies of point defects with charge q as following equation:

$$E^{for}(x^q) = E_x^{N\pm1} - E_{\emptyset}^{N} + \sum_x n_x\mu_x + q(E_{VBM} + \varepsilon_F + \Delta v), (x = \mathrm{Zr},\ \mathrm{Si},\ \mathrm{or\ O}) \quad (1)$$

where $E_x^{N\pm1}$ and $E_{\emptyset}^{N}$ are the total energy of the supercell with and without defect x, respectively. The third term is the chemical potential of atom x with a positive (negative) sign for vacancy (interstitial) defect, and n_x is the number of defect atoms. E_{VBM} refers to the energy of the valence band maximum (VBM) of the defect-free system, and ε_F is the electron chemical potential—i.e., the Fermi energy relative to the VBM, which thus measures from zero to the width of the band gap in the perfect crystal. The shift of the VBM in a defect supercell (Δv) takes the change of the VBM caused by taking the defect into account, whose value can be obtained by a macroscopic average technique [35–37] through determining the difference in the average electrostatic potential between the defect-free and defective supercells.

It is worth noticing that DFT calculations typically underestimate the band gap. The obtained band gap for $ZrSiO_4$ by LDA is 4.512 eV, which is lower by 1.988 eV comparing with experimental value of 6.50 eV [1]. Consequently, we can expect the calculated defect level in the gap to be lower than they would be with a correct band gap according to Eq.(1). Any band correction introduced will consistently shift the formation values upwards. A crude way to account for this problem consists in increasing the formation values by $m \times \Delta E_g$, where ΔE_g is the difference of band gap between theoretical and experimental ones and m corresponds to the number of electrons induced by defects in E_g [38]. Assuming an extra level induced by vacancy is below the conduction band minimum (CBM), its formation energy will be underestimated by 1.988 eV. This situation refers to the case of an O vacancy in $ZrSiO_4$. However, one expects levels that exhibit more valence-band (VB) character to be less affected than those that exhibit more conduction-band (CB) character [38].

According to the thermodynamic equilibrium condition [39], the sum of the chemical potentials of elements (μ_x) must be equal to the heat of formation to ensure the stability of the compound $ZrSiO_4$. In the case of the ternary in $ZrSiO_4$, the μ_x value is determined from equilibrium condition of various phases containing Zr, Si and O atoms. Fig. 1 shows the schematic phase diagram of the ternary system Zr-Si-O. Five points (*A* to *E*) indicated in the diagram correspond to the vertices of the five phase regions. In the assumption that $ZrSiO_4$ is always stable, the chemical potentials of

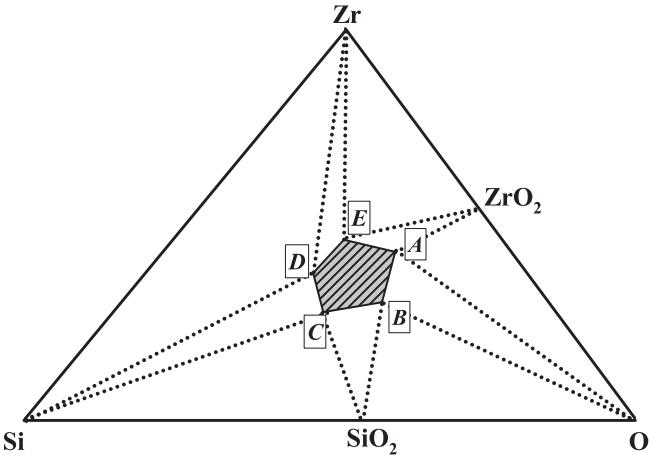

Fig. 1. Schematic phase diagram of the ternary system Zr-Si-O.