First principles study of structural, magnetic and electronic properties of C-doped monoclinic ZrO_2

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ABSTRACT

Structural, magnetic and electronic properties of C-doped monoclinic ZrO_2 have been studied by using the first principles projector augmented wave potential within the generalized gradient approximation as well as taking into account on site Coulomb repulsive interaction. The optimized structures show the lattice constants a, b, c and monoclinic angle β of C-doped monoclinic ZrO_2 change slightly. While the lattice constants a, b, c and monoclinic angle β of C_1-doped monoclinic ZrO_2 are smaller than that of C_2-doped monoclinic ZrO_2. The total magnetic moment of C-doped monoclinic ZrO_2 is mainly contributed by the atomic magnetic moment of C atom. For C atom substituting O atom, the systems are found to be half-metallic material and usable in magnetoelectronic and spintronic devices.

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1. Introduction

As a wide band gap transition metal oxide material, zirconia (ZrO_2) is a very important material due to its outstanding properties such as high dielectric constant, wide optical band gap, high chemical, and thermal stabilities, low optical loss and high transparency in visible and near-infrared regions [1–6]. Because of these properties, it can be found in a wide array of applications in numerous technological and materials fields [7–17]. Zirconia was discovered as baddeleyite early in 1892 by Hussak. Since then, about 10 distinct phases of zirconia have been observed to date experimentally, such as amorphous, metastable tetragonal, monoclinic, tetragonal, cubic structures and so on. Among these ZrO_2 phases, the monoclinic (P2$_1$/c, C_{2h}^5) occurs at temperature from zero to 1180 °C, the tetragonal (P4$_2$/nmc, D_{4h}^{15}) occurs at the temperature from 1180 to 2370 °C and the cubic fluorite (Fm3m, O_h^5) is found at temperature from 2370 to 2600 °C. The temperature in which the tetragonal to cubic transformation occurs can be lowered by the addition of solutes such as MgO, CaO or Y_2O_3, allowing not only the achievement of the stabilized cubic phase even at room temperature but also the production of the materials with extremely high strength, toughness and thermal-shock resistance [18].

Recently, unexpected ferromagnetism called d^0 ferromagnetism has been successively observed in undoped ZrO_2 by Venkatesan et al. [19], which is extremely useful for potential applications in spintronic devices. Crystal structures and properties of the transition metal doped cubic ZrO_2 was experimentally and theoretical studied by several groups [20–23]. At the same time, C substitution has also attracted much attention as potential ways to realize ferromagnetism in ZrO_2 and TiO_2 [24–27]. However, only the total and/or partial (s, p and d) densities of states (DOS) are given out, which can not reveal the spin splitting in ZrO_2. So it is necessary to study the detailed orbital-decomposed electronic structures to check the interaction between the different atoms in doped ZrO_2. In this paper, the structural, magnetic and electric properties of C-doped monoclinic ZrO_2 (m-ZrO_2) are investigated by using the first principles projector augmented wave (PAW) potential within the generalized gradient approximation as well as taking into account the on-site Coulomb repulsive interaction (GGA+U). Owing to the magnetic properties of ZrO_2 with monoclinic structure have been widely studied in past years. The main purpose of this work will be helpful for designing and searching for magnetic properties of semiconductor materials.

2. Calculation methods and models

Using the Vienna ab-initio simulation package (VASP) based on the density function theory (DFT), the calculations are performed

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[28–31]. The electron–ionic core interaction is represented by the projector augmented wave (PAW) potentials [32] which are more accurate than the ultra-soft pseudopotentials. To relax the ions into their ground states, a conjugate-gradient algorithm is used, and the energies and the forces on each ion are converged within 1.0×10^{-5} eV/atom and 0.01 eV/Å, respectively. The cut off energy for the plane-waves is chosen to be 400 eV. The O $2p^4 2s^2$, C $2p^2 2s^2$ and Zr $4s^2 4p^6 4d^2 5s^2$ electrons are treated as valence electrons. The k-point meshes of Brillouin zone sampling in unit cell, based on the Monkhorst–Pack scheme [33], are $11 \times 11 \times 11$ together with a Gaussian smearing broadening of 0.1 eV. The Perdew–Burke–Ernzerhof (PBE) [34] formulation of the generalized gradient approximation taking into account the on-site Coulomb repulsive interaction (GGA+U, $U=2$ eV for Zr) is chosen to treat electron exchange and correlation [35].

The structure of m-ZrO$_2$ (one cell) is shown in Fig. 1(a) with four-formula-unit supercell. As we know, the m-ZrO$_2$ can be described as a distorted fluorite structure with two oxygen sites O$_I$ and O$_{II}$ (O$_I$ where oxygen atom is coordinated to three Zr atoms in an almost planar environment and O$_{II}$ where the central oxygen atom is surrounded by a distorted tetrahedron of four Zr atoms, as shown in Fig. 1(b)). We employ a $2 \times 2 \times 2$ periodic supercell with 96 atoms in which two unit-cell are arranged in each x, y and z directions to avoid the interaction of the doping and its periodic images. Because the two oxygen sites O$_I$ and O$_{II}$ are now nonequivalent, there are two cases for the one C atom substituting one O atom: substituting oxygen in O$_I$ or O$_{II}$ site by carbon, which is marked as C$_1$-doped m-ZrO$_2$ (Fig. 2(a)) or C$_2$-doped m-ZrO$_2$ (Fig. 2(b)), respectively.

3. Results and discussions

The calculated optimized lattice constants and monoclinic angle β of the C-doped m-ZrO$_2$ are listed in Table 1. It can be seen that the lattice constants a, b, c and monoclinic angle β change slightly with one carbon atom substituting oxygen atom comparing with m-ZrO$_2$. Although the electronegativity of 2.55 for carbon is smaller that that of 3.44 of oxygen, the ionic radius of 0.77 Å for carbon is much smaller than that of 1.40 Å for oxygen. We also find the lattice constants a, b, c and monoclinic angle β of C$_1$-doped m-ZrO$_2$ is slightly smaller than that of C$_2$-doped m-ZrO$_2$. This because C$_2$ adjacent four Zr atoms (d_{C_2-Zr}) is consistent with the fact that the interatomic distance increases with increasing coordination number. From the calculation, it is found the obvious magnetic moments of the nearest O and Zr atoms in both C$_1$ and C$_2$-doped structures suggest that the wave function of the C extends to the nearest O and Zr atoms. The atomic magnetic moments of C, O (O where oxygen atom nearest to carbon atom) and Zr (where zirconium atom nearest to carbon atom) are also listed in Table 1. The
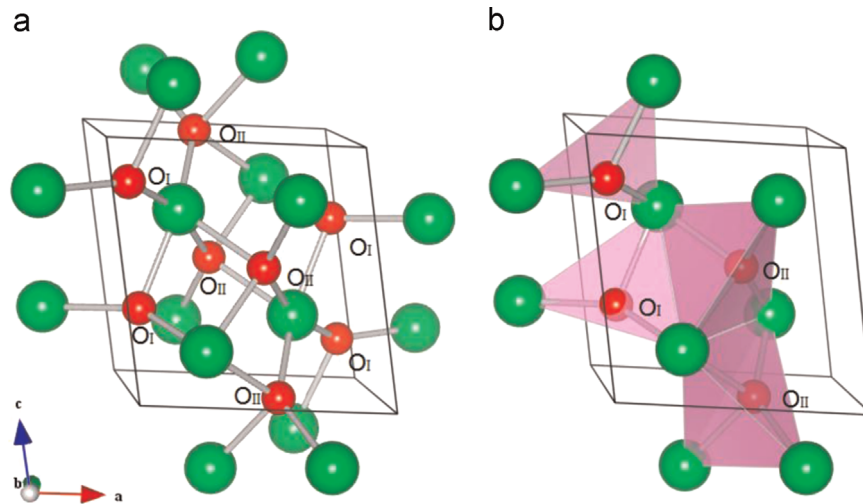

Fig. 1. Crystal structure of m-ZrO$_2$ (a) together with two oxygen sites O$_I$ and O$_{II}$ (b). O$_I$ Where oxygen is coordinated to three Zr atoms in an planar environment and O$_{II}$ where the central oxygen atom is surrounded by a distorted tetrahedron of four Zr atoms.
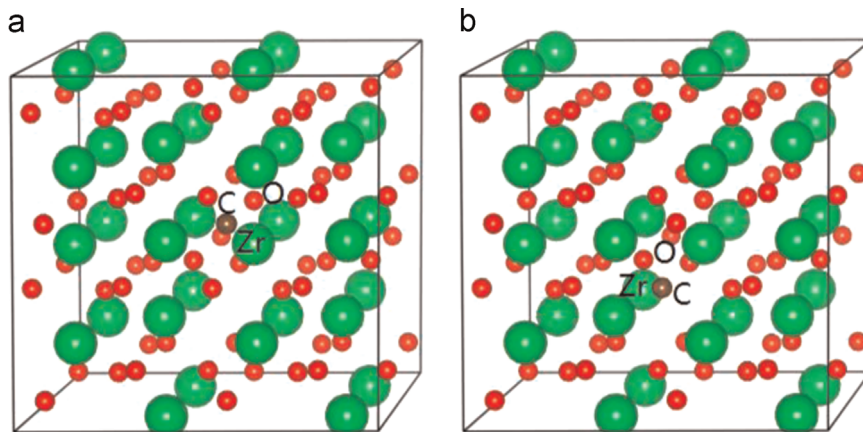

Fig. 2. Crystal structure of C-doped m-ZrO$_2$: (a) substituting O$_I$ atom by C atom(C$_1$) and (b) substituting O$_{II}$ atom by C (C$_2$).