First-principles calculations of electronic and optical properties of C-doped and F, C-codoped cubic ZrO_2

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ABSTRACT

First-principles calculations based on DFT + U were performed on electronic and optical properties of C-doped and F, C-codoped cubic ZrO_2. The calculations show the half-metallic ferromagnetism behaviors of both C-doped and F, C-codoped cubic ZrO_2. Both the direct $2p$–$2p$ interaction and the indirect $2p$–$4d$/$2p$–$2p$ coupling interactions can be expected to contribute to the long-range magnetic coupling. By substitutional codoping of F and C, the band gap is obviously larger than that of C-doped system, because the $2p$ states energies in upper valence band greatly decrease. Meanwhile, F and C codoping induces obvious increase of refractive index and also new steep absorption peaks at lower energy region ~2.5 eV, which can be used for photo absorption applications.

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1. Introduction

As a wide band gap transition metal oxide material, zirconia (ZrO_2) is extensively studied due to its potential applications as high-*k* gate dielectric layers in microelectronic industry, protective coatings, luminophores, oxygen sensors and cathode material in solid fuel cells [1,2]. Recently, unexpected ferromagnetism called d^o ferromagnetism (FM) has been successively observed in undoped ZrO_2 by Venkatesan et al. [3], which is extremely useful for potential spintronics applications. Compared to traditional charge-based semiconductor devices, spintronics devices have attracted great interest due to their unique advantages such as being more powerful, endurable and efficient [4,5]. For use in applications, materials that can both generate and manipulate electronic spin at room-temperature (RT) or above are essential.

At ambient pressure, ZrO_2 exists in three polymorphs: monoclinic structure ($P2_1/c$) at low temperature, tetragonal structure ($P4_2/nmc$) and cubic fluorite structure ($Fm-3m$) at high temperature [6–8]. However, at lower temperatures the cubic phase of ZrO_2 can be stabilized by element doping, such as yttrium. Thus, this phase is in fact the stable structure and can be used in many industrial applications [9,10]. Recently, crystal structures and properties of transition metal doped cubic ZrO_2 was experimentally and theoretical investigated by several groups [11–14]. Meanwhile, C (or N) substitution has also received much attention as

potential ways to realize ferromagnetism in ZrO_2 and TiO_2 [15–17], which challenge the traditional understanding for the origin of ferromagnetism. However, substitutional anion dopants generate oxygen vacancies, and induce band gap narrowing [18]. It was reported that F has a large beneficial effect on charge trapping, and can fill up oxygen vacancies by creating a shallow donor state from the investigations by Schimizu and Koyama [18]. So it can be speculated that codoping of low concentrations of F and C impurities in cubic ZrO_2 could induce a different electronic structure and physical properties that may lead to new applications. It is therefore timely to investigate the electronic structure of these systems. To date, few works have been focused on the electronic and optical properties of F, C-codoped ZrO_2.

For recent years, ZrO_2 based materials have attracted many experimental and theoretical investigations, in which, the method of density functional theory (DFT) has been successfully used in predicting crystal structures and properties of undoped and doped cubic ZrO_2 [12,15,19]. In this paper, we carried out first-principles calculations based on DFT to investigate the electronic structures of both C-doped and F, C-codoped cubic ZrO_2 (denoted *c*-ZrO_2:C and *c*-ZrO_2:F, C) and to find out the probable relations between electronic structure and optical properties.

2. Computational method and details

The first-principles electronic structure calculations based on DFT [20] within CASTEP code [21] were carried out to determine the stability and electronic structures of undoped, C-doped and F, C-codoped cubic ZrO_2. In the calculations, the electron–ionic core interaction is represented by the Vanderbilt ultrasoft

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pseudopotential [22]. The Zr ($4s$, $4p$, $4d$, $5s$), O ($2s$, $2p$), F ($2s$, $2p$) and C ($2s$, $2p$) levels are treated as valence states. To treat electron exchange and correlation, we chose the Perdew–Burke–Ernzerhof formulation of the generalized gradient approximation (GGA–PBE) [23] taking into account the on-site Coulomb repulsive interaction. A cutoff energy of 450 eV for undoped and doped cubic ZrO_2 in the plane wave expansion was employed in the calculations. A $2 \times 2 \times 2$ (or $5 \times 5 \times 5$) Monk-horst–Pack grid [24] was used for integration over the irreducible part of the Brill-ouin zone of the doped cubic ZrO_2 (or undoped system). Good convergence was achieved with the cutoff energy and number of k points. The default convergence criteria of CASTEP was applied within energy tolerance 5.0×10^{-6} eV/atom, max force tolerance 0.01 eV/Å, max displacement tolerance 5.0×10^{-4} Å and max stress tolerance 0.02 GPa. To explore the electronic and optical properties of these solid solutions, we employed a 96-atoms supercell (containing $2 \times 2 \times 2$ full cubic cells) with the starting configuration of cubic ZrO_2 suggested in Ref. [19]. We substituted O atoms by C (or F) atoms to model substitutional C (or F) impurity in cubic ZrO_2, the resulting supercells is $Zr_{32}F_xC_yO_{64-x-y}$ ($x = 0$, 4; $y = 4$).

For the C-doped system, the C concentration is 6.25%, which results from evenly substituting four O atoms with four C atoms in a 96-atoms supercell. There is only one anion site in cubic ZrO_2, so substituting O atom with C needs not consider the site preference. For the F, C-codoped systems, the F concentration is also 6.25%, which results from evenly substituting four O atoms with four F atoms in the 96-atoms C-doped supercell. There are several O sites in C-doped cubic ZrO_2, so substituting O atom with F needs consider the site preference. We model two structures of F, C-codoped cubic ZrO_2, including structure (I) (F and C share a Zr atom at a distance of about 4.47 Å) and structure (II) (F and C share no Zr atom at a distance of about 5.16 Å). Meanwhile, the calculations show that the structure (I) energetically favors over the structure (II) by about 84 meV per F/C. This implies that the admixture of F and C atoms will obviously stabilize the F, C-codoped system.

Within the Broyden–Fletcher–Goldfarb–Shanno (BFGS) scheme [25], geometry optimization was performed allowing both cell parameter and internal coordinates relaxation. In the optical property calculation, the underestimation of the band gap (inherent in DFT calculations) was corrected by introducing a "scissors operator" (2.34 eV), by which the conduction bands positions were raised in energy prior to the interband transition strength calculation to match the general features of the measured imaginary part of dielectric function [26].

The standard DFT formulation usually fails to describe strongly correlated electrons behavior. This limitation can be corrected using the DFT + U method, which introduces a Hubbard parameter "U" for the description of the on-site interactions of those electrons [27]. Considering that the strength of the effective on-site Coulomb repulsion interaction between Zr $4d$ electrons is comparable with the valence bandwidth and the screening of Zr $5s$ electrons, we used the DFT + U methodology with an U value of 2.0 eV to describe the interactions of Zr $4d$ electrons [28,29].

3. Results and discussions

3.1. Structural stability and population analysis

The calculated equilibrium structural parameters and the results of population analysis of undoped, C-doped and F, C-codoped cubic ZrO_2 structures are summarized in Table 1. The calculated equilibrium structural parameter a for cubic ZrO_2 is 5.129 Å, which is in agreement with the experimental value of 5.11 Å [30]. This can demonstrate the applicability of our theoretical model in geometry optimization for ZrO_2. For C-doped cubic ZrO_2, the equilibrium structural parameters a is ~0.55% larger than cubic ZrO_2, which can be explained by the larger radius and lower electronegativity of C atoms compared with O atoms. For F, C-codoped cubic ZrO_2, the equilibrium structural parameters a is basically unchanged compared with C-doped system. From the results of population analysis, it is clearly found that substitutional doping of C will slightly increase the Mulliken charge of O atoms, and decrease the charge of Zr atoms, because C atoms are more likely to donate electrons to Zr than O atoms. From the results, it is interesting to find that substitutional codoping of F and C will greatly decrease the Mulliken charge of C atoms, slightly increase the charge of O atoms, and obviously decrease the charge of Zr atoms. This implies that F and C codoping will obviously enhance the covalent character of Zr—C bond.

Spin-polarized calculations reveal the nonmagnetic character of the undoped cubic ZrO_2. By C doping, a total magnetic moment of ~2.0 μ_B per C is obtained, which nearly equals to the number of holes (1.38 μ_B from C dopant, 0.3 μ_B from its first nearest-neighboring O atoms). Meanwhile, the calculations show that the

magnetic solution energetically favors over the non-magnetic solution by about 371 meV per C, which is even larger than that of Cu-doped ZnO (42 meV), which is known to be FM at RT (RTFM) from the investigations by Buchholz et al. [31]. Therefore, RTFM in C-doped cubic ZrO_2 is possible. In the C-doped system, there are two kinds of Zr atoms, the C-connected Zr (Zr_I) and the C-unconnected Zr (Zr_{II}). The neighboring O atoms of C dopant can be numbered based on their distances from C dopant, including the first nearest-neighboring (NN) O (O_{1NN}), the second NN O (O_{2NN}), the third NN O (O_{3NN-1} and O_{3NN-2}) and the fourth NN O (O_{4NN}) at distances of about 2.60, 3.65, 4.47 and 5.16 Å, respectively. It is found that O_{1NN}, O_{2NN} and O_{3NN-1} atoms share Zr with C dopant, while O_{3NN-2} and O_{4NN} share no Zr with C dopant.

From the calculation, it is found that the obvious magnetic moments of the O_{1NN} atoms suggest that the wave function of the C extends to the O_{1NN} atoms, which are polarized in the same direction with that of the C dopant, hinting strong magnetic coupling occurs between the C dopant and its O_{1NN} atoms. The local magnetic moment may result from the interplay between the strong effective Hund's rule coupling and hybridization [32,33]. In ZrO_2, an O vacancy (O_v) as a donor can introduce two electrons to the system leaving cation dangling bonds. When the C dopant occupies the O_v site, it accepts two electrons to fulfill the C $2p$ orbitals. According to Hund's rules, the substitutional C is left with four $2p$ electrons, which may create 2.0 μ_B per C with a high-spin configuration. Additionally, the O_{3NN-1} atoms also have strong polarization in the same direction with that of the C dopant. This suggests an indirect magnetic coupling interaction mediated by the holes along the C—Zr—O chain. This kind of interaction is induced by the hybridization among the C $2p$, Zr $4d$ and O $2p$ orbitals, and originates from the delocalized nature of the anion $2p$ orbitals compared to the d orbitals of transition metals, and it is strong when the angle of C—Zr—O chain (V_{C-Zr-O}) is 180° ($V_{C-Zr-O3NN-1}$ = 180°). It is also found that the O_{4NN} atoms (sharing no Zr atom with C) have the obvious polarization in the same direction with that of the C dopant. This may suggest that another indirect magnetic coupling interaction is induced by the hybridization among the C $2p$, O_{1NN} and its nearest-neighboring O (at a distance from O_{1NN} ~2.56 Å) $2p$ orbitals, and originates from the delocalized nature of anion $2p$ orbitals, and it is strong when the angle of C—O_{1NN}—O chain ($V_{C-O1NN-O}$) is 180° ($V_{C-O1NN-O4NN}$ = 180°). Taking into account the above results, both the direct $2p$–$2p$ interaction and the indirect $2p$–$4d$/$2p$–$2p$ coupling interaction can be expected to contribute to the long-range magnetic coupling in C-doped cubic ZrO_2.

By codoping of F and C, a total magnetic moment of ~1.0 μ_B per F/C is mostly contributed by the C dopant (0.60–0.66 μ_B) with some contributions from its O_{1NN} atoms (0.12–0.24 μ_B). Meanwhile, the calculations show that the magnetic solutions energetically favor over the non-magnetic solutions by about 61–72 meV per F/C, which are even larger than that of Cu-doped ZnO (42 meV), which is known to be RTFM from the investigations by Buchholz et al. [31]. Therefore, RTFM in F, C-codoped cubic ZrO_2 is possible. In both F, C-codoped structures, there are two kinds of Zr atoms, the C-connected Zr (Zr_I) and the C-unconnected Zr (Zr_{II}). In structure (I), the neighboring O atoms of C dopant can be numbered based on their distances from C dopant, including the O_{1NN}, the O_{2NN}, the O_{3NN} and the O_{4NN} at distances of about 2.62, 3.65, 4.47 and 5.16 Å, respectively. It is found that both O_{1NN} and O_{2NN} atoms share Zr with C dopant, while O_{3NN} and O_{4NN} share no Zr with C dopant. In structure (II), the neighboring O atoms of C dopant can be numbered based on their distances from C dopant, including the O_{1NN}, O_{2NN}, O_{3NN} (O_{3NN-1} and O_{3NN-2}) at distances of about 2.70, 3.65 and 4.47 Å, respectively. It is found that O_{1NN}, O_{2NN} and O_{3NN-1} share Zr with C dopant, while O_{3NN-2} share no Zr with C dopant.