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Performance of cubic ZrO_2 doped CeO_2: First-principles investigation on elastic, electronic and optical properties of $Ce_{1-x}\,Zr_xO_2$

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ABSTRACT

The structural, elastic, electronic and optical properties of $Ce_{1-x}\,Zr_xO_2$ ($x = 0, 0.25, 0.5, 0.75, 1$) fluorite type oxides are studied by researchers using the method of density functional theory (DFT) + U method. The calculated equilibrium lattice parameter, cell volume, elastic and optical properties for CeO_2 and ZrO_2 are all in good agreement with the available experimental data and other theoretical results. It is found that Ce substituted by Zr leads to the formation of the pseudo-cubic fluorite-type structure. With doping concentration × increasing, the lattice parameter, cell volume and the bond length of d_{Ce-O} and d_{Zr-O} decrease linearly. It is interesting to find that the hardness of materials increase with Zr concentration increasing. For $Ce_{0.75}\,Zr_{0.25}\,O_2$, we also find that its ductility is good. **Meanwhile, the range of the conduction band energy in the doped system becomes wider than that in the undoped system.** The overlapping band phenomenon occur for all substitutions in $Ce_{1-x}\,Zr_xO_2$ (from $x = 0.25$ to $x = 0.75$), especially for the structure of $Ce_{0.5}\,Zr_{0.5}\,O_2$ and $Ce_{0.25}\,Zr_{0.75}\,O_2$, its second band gaps almost disappear. Based on the dielectric functions obtained, it is shown that the static dielectric constant ε_0 and refractive index n_0 obviously decrease with Zr concentration increasing. After discussing, we know that CeO_2 is suitable as a useful high-refractive index film material in single and multilayered optical coatings, whereas ZrO_2 can be used as gate-dielectric materials in metal-oxide semiconductor (MOS) devices, in metallurgy and as a thermal barrier coating in engines.

1. Introduction

Ceria (CeO_2) is of great interest in the modern catalytic industry [1–3], due to its wide variety of applications in three-way catalysts (TWCs), high oxygen storage capacity (OSC) and solid oxide fuel cells (SOFCs) [4–6], it is also used in other processes, such as automotive exhaust catalysis and water-gas shift (WGS) reactions [7]. The facility of formation and transportation of oxygen vacancies in CeO_2 are responsible for these technological applications [8]. Although CeO_2 has long been utilized as a material for oxygen storage [4–6,8], it is also found that the CeO_2 is of the potential interest as optical component materials, laser hosts [9]. CeO_2 has been considered as a useful high-refractive index film material in single and multilayered optical coatings [10,11]. **It is can absorb UV efficiently, and it is used as an additive for glass (2–4% CeO_2) to protect light-sensitive materials** [12]. Over the past few years, the optical properties of CeO_2 have been the focus of intensive research [13–16]. Goubin et al. [13] mentioned that ceria **had** a band gap of 3.2 eV, a high UV absorption and a refractive index of 2.35. Niwano et al. [16] have measured the optical reflectance spectra of CeO_2 in the photon energy ranging from 2.5 to 40 eV, and obtained the dielectric and the related functions.

Recently, crystal structures and properties of ZrO_2 doped CeO_2 (the ceria zirconia mixed oxides, $Ce_{1-x}\,Zr_xO_2$) are experimentally and theoretically investigated by several groups [17–25]. Meanwhile, ceria zirconia mixed oxides, $Ce_{1-x}\,Zr_xO_2$ has been paid much attention, for it is used for oxygen storage (release) in three-way catalysts for automotive exhaust treatment [2,6]. The resulting

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$Ce_{1-x}Zr_xO_2$ solid solution facilitates a defective fluorite structure with improved oxygen mobility [26,27]. For example, in experiment, Hosokawa et al. [17] studied the oxygen release capacity of CeO_2-ZrO_2 solid solution by glycothermal method, they found that the oxygen release capacities of CeO_2-ZrO_2 solid solutions synthesized by the glycothermal (GT) method were much larger than those of the samples prepared by a coprecipitation (CP) method. Sanjuán et al. [18] investigated the role of Ce reduction in the segregation of metastable phases in the ZrO_2—CeO_2 system by Raman spectroscopic. Zheng et al. [19] investigated chemical-looping steam methane reforming over macroporous CeO_2-ZrO_2 solid solution, and found that the CeO_2-ZrO_2 mixed oxides calcined at low temperatures (e.g., 450° C) exhibited a better uniform and three-dimensionally ordered macroporous structure, **which enhanced the mobility of oxygen species, and improved the reducibility of CeO_2-ZrO_2 oxygen carriers.** Rodriguez et al. [20] found that Zr mixing $Ce_{1-x}Zr_xO_2$ improved the thermal stability of ceria nanoparticles, but it did not introduce a significant number of oxygen vacancies. They also studied the structural and electronic properties of CeO_2 and $Ce_{1-x}Zr_xO_2$ nanoparticles using time-resolved X-ray diffraction, X-ray absorption near-edge spectroscopy (XANES), and density functional calculations. They found that the lattice constant decreased with Zr content increasing [21]. Nagai et al. [22] analyzed the local structure of CeO_2-ZrO_2 mixed oxides with the same composition ratio, using X-ray absorption fine structure, and they found that the atomically homogeneous $Ce_{0.5}Zr_{0.5}O_2$ solid solution exhibited the highest OSC among these CeO_2-ZrO_2 samples. **Besides, the researchers have also studied** the crystal structures and properties of cubic ZrO_2 doped CeO_2 (the ceria zirconia mixed oxides, $Ce_{1-x}Zr_xO_2$) in theory. Tang et al. [23] investigated the redox properties of M-doped CeO_2 (M = Mn, Pr, Sn, Zr) by using first-principles, and found that the decrease in the O-vacancy formation energy for the Zr-doped CeO_2 was mostly caused by the structural distortion, whereas the decrease for Mn-, Pr-, or Sn-doped CeO_2 originated from the electronic modification as well as from the structural distortion. Yang et al. [24] discussed the effect of Zr doping on the reduction properties of ceria, and found that the Zr dopant had significant **effects** on the ceria structure. Dutta et al. [25] studied the effects of Zr and Ti doping on the dielectric response of CeO_2, and they suggested that the ceria-zirconia mixed oxides should have potential use as high-k materials in the semiconductor industry.

Through above review, we know, though the researchers **have studied** the cerium zirconium oxide **in** theory and experiment of catalytic performance and its related reduction properties, the structural, elastic, electronic and optical properties of cubic ZrO_2 doped CeO_2 (the ceria zirconia mixed oxides) have been less systematical investigations, and the atomic and electronic levels understanding of the properties of the ceria zirconia mixed oxides are still not well understood. These systems maybe induce a different electronic structure and optical properties, which may lead to new applications. Therefore, it is worthwhile to investigate the structural, elastic, electronic and optical properties of these systems. **We carried out first-principles calculations based on density functional theory (DFT) + U method within the generalized gradient approximation (GGA) to investigate the structural, elastic, electronic and optical properties of CeO_2, cubic ZrO_2 and $Ce_{1-x}Zr_xO_2$ (x = 0.25, 0.5, 0.75, the ceria zirconia mixed oxides) in this paper, to find out if, and how, the structural, elastic, electronic and optical properties of CeO_2 are changed as a consequence of cubic ZrO_2 dopant concentrations × in $Ce_{1-x}Zr_xO_2$.**

2. Model and computational details

CeO_2 has a face-centered cubic structure of space group Fm-3m (number 225 in the international tables) [28], it is a rare earth oxide with fluorite-type compound, wherein the Ce atoms are at the corner of the cube and are coordinated by eight equivalent nearest-neighbor oxygen atoms, while the O atoms are tetrahedrally coordinated by four Ce atoms [29,30] [Fig. 1 (a)]. At ambient pressure, ZrO_2 presents polymorphism with cubic (c-ZrO_2), tetragonal (t-ZrO_2, high temperature phases), and monoclinic (m-ZrO_2, stable at room temperature) phases. The cubic ZrO_2 (c-ZrO_2) [Fig. 1(e)] still belongs to the space group Fm-3m, and also has the crystalline structure of fluorite [31]. There are three atoms at the basis in face-centered cubic lattice, with the oxygen atoms at the position (1/4, 1/4, 1/4) and one Zr atom at the position (0,0,0) [32]. For the structure of $Ce_{1-x}Zr_xO_2$ (x = 0, 0.25, 0.5, 0.75, 1), it is also the fluorite oxides that comes from cubic ZrO_2 doped CeO_2. It is a face-centered cubic structure. To study the lattice parameter, elastic, band structure and optical properties of $Ce_{1-x}Zr_xO_2$ (x = 0, 0.25, 0.5, 0.75, 1), the 1 × 1 × 1 supercell with 12 atoms as initial model ([Fig. 1(a–e)] represent the concentration is 0, 0.25, 0.5, 0.75 and 1, respectively.) is adopted, which results from that Zr substitution in CeO_2 is treated using periodic cells of four formula units of CeO_2 with Ce atoms replaced with Zr according to different concentrations of Zr substitution. The first-principles calculations are implemented in the Cambridge Serial Total Energy Package (CASTEP) program [33], based on the density functional theory(DFT) + U method [34], the GGA [35] is used along with ultrasoft pseudopotentials to represent the atoms. Specifically, for geometric optimization, the Perdew-Burke-Ernzerhof potential for solids (PBEsol) is used [36]. The PBEsol method combines the flexibility of the pseudo potential approach with the accuracy of all-electron methods, reproducing the exact valence wave function with all nodes in the core region. Here the cerium 5s, 5p, 5d, 4f, and 6s electrons, zirconium 4s, 4p, 4d, and 5s electrons and the oxygen 2s, 2p electrons electrons are treated as valence electrons [32,37]. Due to the standard DFT formulation usually fails to describe strongly correlated electrons behavior. So we introduce a Hubbard parameter “U” for the description of the on-site interactions of those electrons to correct this limitation [38]. And the gradient-corrected exchange and correlation functionals of the Perdew-Burke-Ernzerhof potential for solids (PBEsol) [36] with the Ce 4f and Zr 4d states that treated with on-site correction for Coulomb interaction (DFT + U) are used in the calculations, based on generalized gradient approximation(GGA) [35,39,40]. Here, we choose 5.0 eV [39] and 2.0 eV [41,42] for the *U* term to describe Ce 4f and Zr 4d states, respectively. The plane-wave basis set cutoff energy is 500 eV [43,44]. The convergence tolerance of energy charge, maximum force and stress are 5×10^{-6} eV, 0.01 eV/nm and 0.02 GPa, respectively [45,46]. Geometry optimization of the initial model in each case is optimized to minimize the total energy using the Broyden, Fletcher, Goldfarb, Shanno (BFGS) method [47]. The Brillouin zones integration is performed by using 4 × 4 × 4 Monkost-Pack grid [43] for the geometry optimization, electronic structure, elastic and optical property calculation of the $Ce_{1-x}Zr_xO_2$ (x = 0, 0.25, 0.5, 0.75, 1).

3. Results and discussion

3.1. Structure stability, population analysis, elastic and electronic properties

3.1.1. Structure stability and population analysis of $Ce_{1-x}Zr_xO_2$

As we all know, CeO_2 has a face-centered cubic structure, it is a rare earth oxide with fluorite-type compound [28], however, ZrO_2 has three phases: cubic (the Fm-3m space group), tetragonal (the $P4_2/nmc$ space group), and monoclinic (the $P2_1/c$ space group). For cubic ZrO_2, it is also attributed to fluorite oxides [31]. Here, we are only interested in cubic fluorite-type structures, and we study some properties of cubic ZrO_2 doped CeO_2 (the ceria zirconia mixed