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First-principles study of noble gas stability in ThO_2

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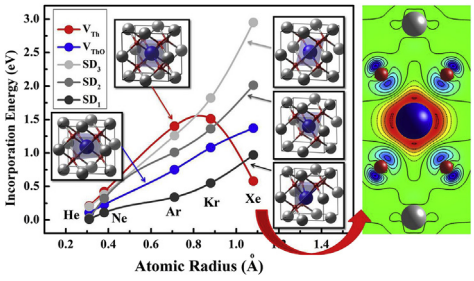
GRAPHICAL ABSTRACT



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ABSTRACT

The stability of noble gases (He, Ne, Ar, Kr and Xe) in thorium dioxide is studied by means of density functional theory. The computations are performed considering insertion sites of ThO_2, including the interstitial sites, the thorium vacancies, the oxygen-thorium di-vacancy and three types of Schottky defects. Our results show that there is an approximately linear relation between the energies and the atomic radii. As the size of the noble gas atom increases, the noble gas atoms energetically prefer to incorporate into large vacancy defects rather than into interstitial positions. Moreover, the binding energy of Kr or Xe interstitial in a Schottky defect is larger than the formation energy of a Schottky defect, suggesting the Schottky defects are thermodynamically favorable in the presence of these noble gas atoms. The charged defects are also considered for noble gas atoms trapped in Th and O vacancies.

1. Introduction

Thorium dioxide is a promising nuclear fuel material for advanced nuclear energy system, such as Molten Salt and high-temperature gas cooled reactors [1]. Compared with UO_2, the most commonly used fuel, thorium dioxide has better radiation resistance and generates negligible plutonium and higher actinides, which advantage the reduction of long-term radiotoxicity of nuclear waste. Moreover, ThO_2 also has greater chemical stability and can be used as an inert matrix for final disposal [2–4]. As the development of the generation IV reactors, which emphasize safety, sustainability and economy, the study of ThO_2 for improving nuclear fuel performance become very attractive and necessary.

A considerable amount of noble gases (NG) are produced in

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nuclear fuels under burning and storage conditions. For instance, krypton and xenon are typical fission products in nuclear fuels, while helium is mainly produced by alpha decay during fuel burn-up. These gases tends to aggregate and form bubbles, which gives rise to fuel swelling and adversely affect mechanical properties of nuclear fuels [5–8]. Hence it would be of great interest to understand the behavior of noble gases in nuclear fuels. Due to the difficulties in experiments, there is a need for reliable theoretical calculations of defect energy, which associates with the formation of noble gas bubbles. Density functional theory (DFT) has been proved an effective method to evaluate point defect energies in atomic-scale calculations [9–13]. In recent years, a number of theoretical investigations are concerned with bulk properties and defects behavior of nuclear fuels [14–25]. P Zhang et al. [14,15] calculated the thermodynamic properties and structural stability of thorium dioxide from the first-principles study. Nerikar et al. [16,17] studied the stability of selected fission products including Xe in $UO_{2\pm x}$ using spin-polarized GGA+U. The most stable solution site of Xe was found to be the Schottky defects for UO_{2-x} and UO_2, and the uranium vacancy for UO_{2+x}. Yun et al. [19,20] reported that xenon has a lower mobility in ThO_2 than in UO_2, due to the strong resistance against oxidation of ThO_2. Thompson et al. [25] noted that the stability of noble gases in UO_2 has strong dependence on the volume of the noble gas atom, corresponding to the strain it causes in the interstitial site. Most researches have focused on the noble gas behavior in UO_2, while similar effects in ThO_2 matrix is relatively unknown.

In this work, we study a series of noble gases, He, Ne, Ar, Kr, and Xe in ThO_2, aiming to a systematic understanding of their behaviors. Firstly, the numerical methodology employed in the present work is described. Then the structures and supercell volume variations are calculated. At last, the incorporation and solution energies of noble gas atoms in trap sites are calculated and the stability mechanism of noble gas atoms is discussed.

2. Methodology

The calculations were performed under the framework of density functional theory as implemented in the Vienna ab initio simulation package (VASP) [26–29]. The projected augmented wave method (PAW) [30] and the generalized gradient approximation (GGA) [31] were used. The exchange and correlation energies were calculated using the Perdew–Burke–Ernzerhof (PBE) functional [32]. The wave functions were expanded in a plane-wave basis set with an energy cutoff of 500 eV. Since ThO_2 is a diamagnetic material [15], the spin polarization was not considered in the calculation. The results were also checked with spin polarized calculations, which make no obvious differences. According to previous studies [14,33,34], the spin-orbit interaction induces little modifications on the electronic structures and lattice constants of ThO_2. Therefore, the spin-orbit interaction is not considered in this study. Moreover, since thorium contains no occupied 5f states, the strong correlation effect of ThO_2 is negligible. It has been reported [14,19,35] that the GGA approximation can give nearly correct energy information for ThO_2, and therefore the GGA+U method [24,36] was not adopted in this work. The lattice constants and internal freedom of the unit cell were fully optimized until the Hellmann-Feynman forces on the atoms were less than 0.01 eV/Å. The effective charge for each atom was calculated using Bader charge analysis [37].

In order to simulate the noble gas atoms incorporated in ThO_2, a $2 \times 2 \times 2$ supercell is used in the calculation, containing 96 atoms. According to previous results [35,36], a supercell of this size has been proven to make the energies sufficiently converged. Depending on the unit cell size and shape, a $2 \times 2 \times 2$ Monkhorst–Pack sampling mesh [38] of k-points was used. All these calculation were checked using larger energy cutoffs and k-meshes; the results of total energy and Hellmann-Feynman forces were converged within 0.01 eV and 0.01 eV/Å, respectively.

3. Results and discussion

ThO_2 crystallizes in a cubic fluorite structure with a non-magnetic ground state. The PBE calculated lattice constant is 5.62 Å, which is in agreement with the experimental lattice constant of 5.60 Å [39–41]. In contrast, the LDA calculated value is 5.53 Å. Since the PBE calculations in this paper result in a lattice constant that is closer to the experimentally determined one, the PBE functional is used for further calculations.

To investigate the behavior of noble gases in ThO_2, the following trap sites are considered: the octahedral interstitial defect (Int.), the thorium vacancy (V_{Th}), the oxygen-thorium di-vacancy (V_{ThO}) and the Schottky defect (SD). For the SD clusters, one thorium atom and two neighboring oxygen atoms are removed from the lattice. Three configurations for the constituent vacancies for this defect are considered, assuming each oxygen vacancy is the nearest neighbor of the thorium vacancy. These three SD clusters differ by the distance between the two oxygen vacancies. The three configurations are noted as the first-(SD_1), second-(SD_2), and third-(SD_3) nearest-neighbor oxygen vacancies [42,43], as shown in Fig. 1.

When noble gas atoms are introduced in the supercell structure, the volume of the structure varies according to different doping sites and types of dopant atoms. This volume modification is denoted as

$$\Delta V = V_{NG}^{X} - V \tag{1}$$

where V_{NG}^{X} is the volume of the supercell with incorporation of the noble gas in trap site X (defect), and V is the volume of supercell without defects. The volume variations induced by the defects are listed in Table 1. There is almost no volume change for the incorporation of He in the interstitial sites. As the size of noble gas atom increases, the supercell volume increases correspondingly. In the cases of SD sites, for He and Ne, the maximum $\Delta V/V$ values do not exceed 0.5% (0.4% for He, 0.5% for Ne). The largest volume variation for Ar, Kr and Xe occurs in interstitial sites. Kr and Xe interstitials in ThO_2 induce a relatively large swelling of the supercell and $\Delta V/V$ is roughly 1.5% and 2.3%, respectively. When these large noble gas atoms are trapped by vacancies, the volume variation decreases as expected. Note that the smallest volume variation for Xe and Kr is in the thorium vacancy, while it is in the SD_1 site for Ar. Overall, the volume variations induced by noble gas dopants are all under 1.5%, except for Xe in interstitial sites (2.3%). Since our calculations mainly focus on the properties of vacancies in ThO_2, the small volume variations (<1.3%) in Table 1 indicate that the size of the supercell is sufficiently large.

The incorporation energy E_{NG-X}^{Inc} is defined as the energy required to incorporate an atom in a pre-existing defect site:

$$E_{NG-X}^{Inc} = E_{NG}^{X} - E^{X} - E_{NG}, \tag{2}$$

where E_{NG}^{X} and E^{X} are the total energies of the system with and without incorporation of the noble gas in trap site X, and E_{NG} is the total energy of an isolated noble gas atom. The calculated incorporation energies are shown by Table 2 and Fig. 2.

First we note that the incorporation energies of noble gas into interstitial sites are apparently larger than those in vacancy-type defects. The incorporation energies become larger for larger noble gas atoms. For instance, it takes 0.75 eV to incorporate the helium into an interstitial site while 9.94 eV for xenon. Different values of