



## Energetics of halogen impurities in thorium dioxide



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### ABSTRACT

Defect energies for halogen impurity atoms (Cl, Br and I) in thoria are calculated using the generalized gradient approximation and projector augmented plane wave potentials under the framework of density functional theory. The energy to place a halogen atom at a pre-existing lattice site is the incorporation energy. Seven sites are considered: octahedral interstitial, O vacancy, Th vacancy, Th-O di-vacancy cluster (DV) and the three O-Th-O tri-vacancy cluster (NTV) configurations. For point defects and vacancy clusters, neutral and all possible defect charge states up to full formal charge are considered. The most favourable incorporation site for Cl is the singly charged positive oxygen vacancy while for Br and I it is the NTV1 cluster. By considering the energy to form the defect sites, solution energies are generated. These show that in both ThO<sub>2-x</sub> and ThO<sub>2</sub> the most favourable solution equilibrium site for halides is the single positively charged oxygen vacancy (although in ThO<sub>2</sub>, I demonstrates the same solubility in the NTV1 and DV clusters). Solution energies are much lower in ThO<sub>2-x</sub> than in ThO<sub>2</sub> indicating that stoichiometry is a significant factor in determining solubility. In ThO<sub>2</sub>, all three halogens are highly insoluble and in ThO<sub>2-x</sub> Br and I remain insoluble. Although 1/2Cl<sub>2</sub> is soluble in ThO<sub>2-x</sub> alternative phases such as ZrCl<sub>4</sub> exist which are of lower energy.

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## 1. Introduction

The incorporation of impurity atoms in a ceramic can have a strong influence on the chemical, mechanical, optical and diffusional properties of the material [1,2]. The eventual location of impurity atoms, be that through incorporation via chemical doping or ion implantation or fission, depends on the relative and absolute site solution energies. Much effort has been expended to study the effect of impurity atoms on the properties of ceramic materials [3,4]. However, the effect of impurity atoms in materials that are being used or proposed to be used in nuclear reactors, especially as fuels, is less well understood, mainly due to their radiotoxicity, making experimental studies especially challenging [5]. Here, we have considered thoria (stoichiometric ThO<sub>2</sub> and substoichiometric ThO<sub>2-x</sub>), a prospective ceramic nuclear fuel, especially in the form of (Th,U)O<sub>2</sub> and (Th,Pu)O<sub>2</sub> mixed oxides (MOX) [6]. Burn-up of the fissile isotopes of MOX fuels generates many radioactive volatile fission products (e.g., Kr, Xe, Cl, Br, I, Cs, Rb, Te) [7]. The inert gasses

(Kr, Xe) degrade mechanical properties (by causing swelling of fuel pins, the development of micro cracks and void formation [7,8]) and thermal properties (by reduction of thermal conductance in fuel-clad gap [9]). Volatile halogens are produced in smaller quantities (compared to gaseous fission products) and are also present in fuel as impurity atoms but their high electro-negativity means they are especially reactive, leading to detrimental chemical interaction with the fuel. They also cause the eventual degradation of mechanical properties through stress corrosion cracking and brittle fracture of the clad [8,10]. Thus, it is important to establish the solution energies and site preferences of halogens in the fuel matrix and their chemical interactions with the fuel.

Despite the important chemical interactions of impurity halogens with ceramic nuclear fuels, few literature studies consider the issue. Nevertheless, experimental studies have been reported for halogen generation and diffusion in urania especially since chlorine (<sup>35</sup>Cl: 75.77% and <sup>37</sup>Cl: 24.23%) is present as an impurity (<0.5 ppm) in urania and urania based MOX, prior to reaction operation. During reactor operation, <sup>36</sup>Cl is produced by neutron capture due to the <sup>35</sup>Cl(n, γ)<sup>36</sup>Cl reaction, which exhibits a high cross-section for thermal neutrons [11,12]. Cl<sub>2</sub> has to be considered as it is volatile

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and  $^{36}\text{Cl}$  in particular given its long half-life ( $3.01 \times 10^5$ ) years. A number of investigations into the release and diffusion of iodine and other volatile fission products (Xe, Te, Cs) have also been reported [13–15], using gamma-ray and secondary ion mass spectrometry.

Generally, experimental studies describe macroscopic phenomena rather than explaining the basic atomic scale incorporation and diffusion mechanisms of impurity halogens and linking this to their effects on material properties. Atomic scale computer simulation predictions of solution energies and site occupancies in nuclear materials therefore provide useful complementary information to help understand macroscopic observations (be that of the fuel or clad cracking). Moreover, the use of  $^{232}\text{ThO}_2$  based MOX as a reactor fuel in place of urania based MOX is relatively new [6,7]; as a result, no previous experimental studies of halogen solution and migration in thoria have been reported.

Atomic scale density functional theory (DFT) based calculations have provided understanding of basic point defect behaviour in solids for over a decade [1]. Especially for urania, DFT based approaches have been used to predict the behaviour of point defects (vacancies and self-interstitials) and the effects of impurities (He, Kr, Xe, I, Cs, Sr etc.) in urania [16–20]. Conversely, thoria has been less well studied. Some atomic scale modelling studies on trapping and diffusion of the volatile fission products (Xe, Br, Rb and Cs) [18,20] have been reported but these only considered the incorporation of impurity atoms in neutral point defects and neutral clusters of defects, leaving aside the possibility of incorporation in charged defect configurations. A more extensive study of Xe and Kr has been made [21], which did consider charged as well as neutral defect sites. This also considered solution in stoichiometric  $\text{ThO}_2$  and substoichiometric  $\text{ThO}_{2-x}$ .

The study here focuses on the stability and chemical interaction of halogen impurity atoms (Cl, Br and I) in thoria by considering seven incorporation sites for these atoms: the octahedral interstitial, O vacancy, Th vacancy, Th-O di-vacancy cluster (DV) and the O-Th-O neutral tri-vacancy cluster (NTV) (for which there are three configurations [21]). For point defects and vacancy clusters, both neutral and all charged defect configurations, up to full formal charge, are considered for the calculation of incorporation energies (i.e. the energy to place a halogen ion on a pre-existing defect site). The most probable incorporation site for a halogen impurity is that with the lowest incorporation energy. This assumes that the concentration of defect sites is greater than the concentration of halogen ions. Incorporation energies are then used as the basis for calculating solution energies by considering the energy to form the defect (trap) site. This assumes that the concentration of halogen ions is greater than the availability of defect sites (which is appropriate for all but the very lowest defect concentrations [21]). The effect of van der Waals (vdW) interactions is considered and included for all possible defect configurations.

## 2. Theoretical methods

### 2.1. Calculation models

$\text{ThO}_2$  exhibits a face-centered cubic fluorite type crystal structure. We used the conventional cell of  $\text{ThO}_2$  ( $\text{Th}_4\text{O}_8$ ) to calculate the equilibrium lattice parameters and electronic properties. In order to calculate defect formation energies and the interaction of halogens with these defects, we used a  $2 \times 2 \times 2$  supercell containing 96 atoms. Fig. 1 shows the seven defect sites considered in this study.

### 2.2. Calculation methodologies

The calculations were carried out using the spin-polarized mode

of density functional theory as implemented in the VASP package [22,23]. The exchange-correlation term was modelled using the generalized gradient approximation (GGA) parameterized by Perdew, Burke, and Ernzerhof (PBE) [24]. The standard projected augmented wave (PAW) potentials [25] and a plane-wave basis set with a cut off value of 500 eV were employed. The valence electronic configurations for Th, Cl, Br, I and O were  $6s^2 6p^6 6d^2 7s^2$ ,  $3s^2 3p^5$ ,  $4s^2 4p^5$ ,  $5s^2 5p^5$  and  $2s^2 2p^4$  respectively. In order to describe the behaviour of the localized Th *f* states we included the orbital-dependent, Coulomb potential (Hubbard U) and the exchange parameter J within the DFT + U calculations, as formulated by Liechtenstein et al. [26]. We applied the values of  $U = 4.5$  eV and  $J = 0.5$  eV to the localized *f* states of Th. Charged defects interact with their next periodic images. In our previous study [21] we described the methodology as implemented by Makov et al. [27] to compensate for image charges when calculating defect formation energies.

A  $2 \times 2 \times 2$  supercell containing 96 atoms was used for the defect calculations. A  $2 \times 2 \times 2$  Monkhorst-Pack [28] *k* point mesh, which yielded 8 *k* points was used in all calculations. Structural optimizations were performed using a conjugate gradient algorithm [29] and the forces on the atoms were obtained from the Hellman-Feynman theorem including Pulay corrections. In all optimized structures, forces on the atoms were smaller than 0.001 eV/Å and the stress tensor was less than 0.002 GPa.

Halogen atoms and diatomic halogen molecules were relaxed in a 12 Å periodic cubic cell using only one *k* point (gamma point). We use both the energies of a halogen atom and half the total energy of a molecule to calculate incorporation energies.

The inclusion of van der Waals (vdW) interactions is particularly important for the incorporation of highly polarizable halogen atoms into  $\text{ThO}_2$ . In this work, dispersion has been included by using the pair-wise force field as implemented by Grimme et al. [30] in the VASP package.

In previous work [21] we partially demonstrated the validity of the parameters by showing the good correspondence between predicted and experiment values for lattice constants and bulk modulus for Th and  $\text{ThO}_2$ .

### 2.3. Definition of energetics

Bond dissociation energies (BDE) for diatomic halogen molecules were calculated using the following equation:

$$\text{BDE} = 2E[X] - E[X_2] \quad (1)$$

where  $E[X]$  is the energy of halogen atom and  $E[X_2]$  is the energy of diatomic halogen molecule.

The incorporation energy of a halogen atom in the octahedral interstitial site was calculated using the following equation:

$$E[X_i] = E[X_i\text{Th}_n\text{O}_{2n}] - E[\text{Th}_n\text{O}_{2n}] - E[X] \quad (2)$$

where  $E[X_i\text{Th}_n\text{O}_{2n}]$  is the energy of a halogen atom incorporated into a  $\text{ThO}_2$  supercell,  $E[\text{Th}_n\text{O}_{2n}]$  is the total energy of the defect-free  $\text{ThO}_2$  supercell and  $E[X]$  is the energy of a single halogen atom. The incorporation energy of a halogen atom at a defect site, for example I at an oxygen vacancy site, is given by,

$$E[I(V_O)] = E[I_O\text{Th}_n\text{O}_{2n-1}] - E[\text{Th}_n\text{O}_{2n-1}] - E[I] \quad (3)$$

where  $E[I_O\text{Th}_n\text{O}_{2n-1}]$  is the total energy of the supercell containing an I atom at an oxygen vacancy and  $E[\text{Th}_n\text{O}_{2n-1}]$  is the total energy of the cell containing an unoccupied oxygen vacancy.

Relative incorporation energies are important because

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