



Point defects and non-stoichiometry in thoria



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ABSTRACT

Thoria is a possible alternative to urania as a nuclear fuel. In order to adopt thoria it is necessary to gain a thorough understanding of the defect processes that control its macroscopic properties. Here we perform density functional theory simulations coupled with chemical potentials calculated using simple thermodynamics, to explore the defect chemistry in ThO_2 over a wide range of temperatures and oxygen partial pressures. The results predict the hypostoichiometric, ThO_{2-x} , regime to be characterised by V_O^{2+} defects charge compensated by conduction band electrons. The simulations also highlight the importance of the poroxo-oxygen interstitial defect, which is predicted to form with a significantly higher concentration than octahedral oxygen interstitial defects under hyperstoichiometric, ThO_{2+x} , conditions. Despite this thoria is not expected to accommodate a significant oxygen excess, which agrees with experimental observations.

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1. Introduction

Thoria, ThO_2 , has a number of important industrial applications, the most promising of which is as a possible replacement for UO_2 in nuclear reactors. As a nuclear fuel, fission products generated during the fission process must be accommodated at point defects in the fuel matrix. Consequently, it is necessary to understand the underlying defect chemistry. As Th isotopes are fertile but not fissile, thoria fuel is usually doped with small quantities (<20% of the dopant) of either ^{233}U , ^{235}U or ^{239}Pu to generate mixed oxide (MOX) fuels [1]. The incorporation of the uranium or plutonium species modifies the defect chemistry of the fuel, which coupled with the random arrangement of the cations in MOX makes understanding its defect chemistry complex. An essential step in understanding defect processes in mixed oxide fuels is to understand the defect chemistry occurring in the end members UO_2 , PuO_2 and ThO_2 .

As is the case for other fluorite oxides, such as CeO_2 , thoria displays high oxygen ion conductivity; however, its high radioactivity toxicity renders it unsuitable for use in a solid oxide fuel cell. In oxygen conducting materials the dominant disorder type arises due to the oxygen Frenkel process. Under stoichiometric conditions and assuming that defects exist in their fully ionic charge state this can be expressed in modified Kröger–Vink notation as:



where O_O^\times is an oxygen atom on its native lattice site, O_i^{2-} is a doubly negatively charged oxygen ion residing at an interstitial site and V_O^{2+} corresponds to an oxygen vacancy defect where the two electrons localised on the oxygen ion have also been removed. If we apply the law of mass action, the equilibrium constant, k_1 , for reaction 1 is $[\text{O}_\text{i}^{2-}] = [\text{V}_\text{O}^{2+}] = k_1^{\frac{1}{2}}$. Electron and electron hole defects can be created by the thermally activated promotion of an electron from the valence to the conduction band, i.e.



As the band gap in solid ThO_2 is large (5.75 eV) [2] the equilibrium constant for reaction 2, k_2 is significantly lower than k_1 , i.e. $k_1 \gg k_2$.

At oxygen partial pressures greater than that required to maintain stoichiometry $[\text{O}_\text{i}^{2-}] \gg [\text{V}_\text{O}^{2+}]$, the defect reaction is:



and the equilibrium constant for this reaction, $k_3 = [\text{O}_\text{i}^{2-}] \cdot [h^{1+}]^2 \cdot p_{\text{O}_2}^{-\frac{1}{2}}$. Employing the electroneutrality condition $2[\text{O}_\text{i}^{2-}] = [h^{1+}]$ the concentration of the dominant electron hole defects is proportional to $p_{\text{O}_2}^{\frac{1}{4}}$, such that,

$$[h^{1+}] = 2 \left(\frac{k_3}{4} \right)^{\frac{1}{3}} p_{\text{O}_2}^{\frac{1}{4}}. \quad (4)$$

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A similar approach may be adopted to examine oxygen deficient ThO₂, where $[V_{O}^{2+}] \gg [O_i^{2-}]$ and the defect reaction given by



and the electron concentration may be calculated from

$$[e^{1-}] = 2[V_o^{2+}] = 2(k_5)^{\frac{1}{2}}p_{O_2}^{-\frac{1}{2}} \quad (6)$$

indicating a $p_{O_2}^{-\frac{1}{2}}$ dependence [3].

Based on Eqs. (4) and (6) the conductivity of ThO₂ would be expected to display a $p_{O_2}^{\frac{1}{2}}$ and $p_{O_2}^{-\frac{1}{2}}$ dependence for high and low partial pressures respectively. A number of authors have examined the partial pressure dependency of the conductivity of ThO₂. At high oxygen partial pressures (i.e. $> 10^{-6}$ atm) Bauerle predicts that the conductivity increases with a $p_{O_2}^{\frac{1}{2}}$ dependence [4]. This was explained by invoking the following reaction:



where the presence of vacancies is anticipated to arise due to the presence of impurities such as Ce³⁺. Bransky and Tallan argue that the $[h^{1+}]p_{O_2}^{\frac{1}{2}}$ dependence arises due to performing the measurement of the conductivity over a narrow range of oxygen partial pressures, where the conductivity is characterised by the neutrality condition $[h^{1+}] + 2[V_o^{2+}] = [F_{Th}^{1-}] + 2[O_i^{2-}]$ where F is a trivalent dopant located on a Th site [5]. The width of this region depends on the relative mobility of the oxygen and hole defects. As the mobility of the electron holes is expected to be much greater than for oxygen ions, they expect the onset of the *p*-type conductivity and hence a $[h^{1+}]p_{O_2}^{\frac{1}{2}}$ region occurs at partial pressures towards the top of the equality $[h^{1+}] + 2[V_o^{2+}] = [F_{Th}^{1-}] + 2[O_i^{2-}]$. A similar argument has been proposed by Ando and Oishi [6]. Beyond this region both studies predict that the equality $[h^{1+}] = 2[O_i^{2-}]$ will become dominant; however, they acknowledge that it is very difficult to generate samples pure enough to observe the simple non-stoichiometric regime.

At lower oxygen partial pressures the conductivity is shown to be independent of the oxygen partial pressure (implying ionic conduction) until there is evidence of *n*-type conductivity at very low oxygen partial pressures [5,7]. The width of the region of ionic conductivity is observed to decrease with increasing temperature due to the rapid increase in *n*-type conduction [5,7].

The *n*-type conductivity dependency on the partial pressure is hard to characterise due to the difficulties of achieving equilibrium under such reducing conditions; however, Bransky and Tallan [5] predict a $p_{O_2}^{-\frac{1}{2}}$ dependence whilst Choudhury and Patterson predict either a $p_{O_2}^{-\frac{1}{2}}$ or $p_{O_2}^{-\frac{1}{3}}$ [7] dependency on the oxygen partial pressure.

Atomistic simulation techniques, especially first principles methods such as density functional theory (DFT), facilitate the study of point defects, specifically through the calculation of defect formation energies. Using simple thermodynamics, defect formation energies may be determined, parameterised by chemical potentials for each species that may be added or subtracted to create defects. Specific values of the chemical potentials can then be linked to different stoichiometry regimes and environmental conditions, thereby allowing the calculation of the concentrations of the defects under different conditions. Furthermore, the simulations allow us to explore the influence of dopants on the defect concentrations as well as the role of the defects not in their full valence charge states. Thus, here we will employ DFT to calculate defect formation energies for the intrinsic defects in thorium for all likely charge states with the aim of creating Brouwer diagrams showing its defect chemistry across a range of experimentally relevant conditions.

These results will also allow us to discuss the solubility of the different fission products that will be presented in future work.

2. Methodology

2.1. Defect formalism

Within the point defect model, the concentration, c_i , of defect i can be related to the change in the Gibbs free energy, ΔG_f^i , to form the defect, i , that is,

$$c_i \propto m_i \exp\left(\frac{-\Delta G_f^i}{k_B T}\right) \quad (8)$$

where, m_i is the multiplicity of equivalent sites, k_B is the Boltzmann constant and T is the temperature. A more complex expression for c_i has been derived by Kasamatsu et al. which considers like defects with different charge states competing for the same sites; however, in general the defect concentrations are sufficiently low in ThO₂ that this will have no effect on the resulting defect chemistry [8]. At the temperatures relevant to solids, the difference in vibrational contributions to the free energy between perfect and defect supercells is expected to be negligible so we can approximate ΔG_f^i by ΔE_f^i , calculated from the differences in total energies between perfect and defective cells according to the formalism of Zhang and Northrup [9]. Recently, Youssef and Yildiz have suggested that this approximation may not hold at high temperatures [10]. The defect formation energy is then given by:

$$E_f = E_{\text{defect}}^T - E_{\text{perf}}^T + \sum_{\alpha} n_{\alpha} \mu_{\alpha} + q_i \mu_e + dE, \quad (9)$$

where E_{defect}^T and E_{perf}^T are the DFT total energies of the system with and without the defect respectively, n_{α} is the number of atoms added/removed, μ_{α} is the chemical potential of the species α that is added/removed, q_i is the effective charge on the defect and $\mu_e = E_{\text{VBM}} + \varepsilon_F$. E_{VBM} is the energy of the valence band maximum (VBM) and ε_F is the electron chemical potential above the VBM. dE is a correction used to mitigate the interactions of the defect charges with their periodic images. Here we employ a Madelung correction as proposed by Leslie and Gillan [11] employing the experimental dielectric constant of 18.9 [12].

In a crystal, the sum of the concentrations of ionic and electronic defects, each multiplied by their charges, must balance to produce overall charge neutrality. This can be expressed as:

$$\sum_i q_i c_i - N_c \exp\left(-\frac{E_g - \varepsilon_F}{k_B T}\right) + N_v \exp\left(-\frac{\varepsilon_F}{k_B T}\right) = 0 \quad (10)$$

where the first term is simply the sum of the charges of the ionic defects and the second and third terms correspond to the electron and hole concentrations respectively. N_c and N_v are the effective conduction band and valence band density of states and E_g is the bandgap. Boltzmann rather than Fermi-Dirac statistics have been employed for the electron and hole populations as in an insulating material they are expected to be sufficiently low that this approximation holds accurately within the stoichiometry and temperature ranges considered. As Eq. (10) shows, the formation energy for an electron in the conduction band is approximated to be equal to $E_g - \varepsilon_F$. In reality the formation energy will be slightly lower due to self-trapping of the electrons; however, it is a reasonable approximation to use E_g in a wide bandgap insulator such as ThO₂ [13].

Using the framework described above, a Brouwer diagram can then be constructed by determining the electron chemical potential that ensures charge neutrality for any given chemical potentials and calculating the concentrations of the individual defects. We note that all defects studied here are considered to be in the dilute limit so that

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