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Configurational analysis of uranium-doped thorium dioxide

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Abstract While thorium dioxide is already used industrially in high temperature applications, more insight is needed about the behaviour of the material as part of a mixed-oxide (MOX) nuclear fuel, incorporating uranium. We have developed a new interatomic potential model, commensurate with a prominent existing UO_2 potential, to conduct configurational analyses of uranium-doped ThO_2 supercells. Using the GULP and Site Occupancy Disorder (SOD) computational codes, we have analysed the distribution of low concentrations of uranium in the bulk material, but have not observed the formation of uranium clusters or a single dominant configuration.

1. Introduction

Although the majority of nuclear power reactors operating today use uranium and/or plutonium-based fuels such as low-enriched uranium (LEU) or mixed oxide fuels (MOX), alternative nuclear fuels are being considered as well.[1] Thorium compounds can be used to fuel nuclear reactors and they present an attractive alternative to the standard uranium and plutonium-MOX fuels. As many countries around the world rethink their nuclear energy programs in the wake of the Fukushima event, interest in thorium energy is growing as a result.[2]

While thorium is a fertile material, it is not fissile and therefore a sustained conversion to the fissile ^{233}U isotope can only occur in the presence of a neutron source. Although plutonium and uranium may serve as the source, there are several advantages to blending thoria with uranium that have been confirmed experimentally, including changes in the decay heat, melting point, and thermal conductivity of the material, in addition to a decrease in the release rate of fission gases despite an actual increase in the production of fission gases.[3]

Since a small amount of a neutron source is required for application as a nuclear fuel, it is useful to study thorium dioxide (thoria) in the context of uranium-doping. Pure thoria is a ceramic material with a melting point of 3651 K, the highest of any known oxide.[4] Unlike uranium and plutonium oxides, ThO_2 also represents the highest oxidation state of the material, which makes it exceptionally stable in the presence of oxygen or oxygenated water. This corrosion resistance has positive implications for the use of thoria in nuclear fuels.[3]

Thoria has the fluorite structure, space group $Fm\bar{3}m$ (225), which is shared with the dioxides of, for example, cerium, plutonium, and uranium. As ThO_2 and UO_2 are isostructural and blends of the



two materials are combined to form nuclear fuels, there is significant interest in thorium-uranium solid solutions, both experimentally and theoretically.

2. Methodology

To investigate the distribution of uranium atoms in thorium, a 96-atom 2x2x2 thorium supercell was used as the base material. The oxygen-oxygen interaction is described by the potential published by Catlow, whereas initial values of A and ρ were taken from the Catlow U-O Buckingham potential.[5] Due to the similarities between uranium and thorium, these values provided a good starting point for the derivation of a Th-O potential, which is described by a Buckingham equation:

$$V = A \exp(-r/\rho) \quad (1)$$

where $A = 1281.775$, $\rho = 0.391$

We have next used this ThO₂ potential along with the leading Catlow UO₂ potential in the Site-Occupancy Disorder (SOD) code, version 0.26.[6] to obtain the distribution of uranium in a range of concentrations in the thorium lattice. The SOD code takes advantage of internal symmetry operators in the material to reduce the total number of possible configurations for a given substitution to only the number of independent configurations.

For a uranium-substituted 2x2x2 supercell of Th_(32-x)U_xO₆₄, where x ranges from 2-5, the number of these inequivalent configurations was determined with SOD, followed by energy minimizations under constant pressure using Gulp 3.4.[7,8] The resulting energies of each of the independent configurations was compared to pure thorium to determine the most energetically favourable distributions of uranium atoms in the system.

Additionally, the SOD code was used to determine the Boltzmann probabilities of the non-equivalent configurations.[6,9] The probability P_m of each independent configuration, m , is calculated according to equation 2, where G_m is the vibrational free energy, Ω_m represents the number of times the independent configuration occurs in the total configurational space, k_b is Boltzmann's constant, and Z is the partition function:

$$P_m = \frac{1}{Z} \Omega_m \exp\left(-\frac{G_m}{k_b T}\right) \quad (2)$$

3. Results

The SOD code identified five independent configurations in the Th_(32-x)U_xO₆₄ supercell where $x=2$, whereas there are 14 for $x=3$. These systems represent concentrations of approximately 6% and 9% uranium, respectively, which is in line with real-world fuel applications of doped thorium. For each value of x , the energy differences between the lowest and highest configurations were less than 0.1 eV. As a result, the Boltzmann probability distributions illustrated in Figure 1 indicate that there is not one dominant configuration for $x=2$ or $x=3$. In all cases, the lack of one dominant configuration indicates that the system is disordered. However, by comparing the probabilities and the configurational energies, it is noted that those configurations with the highest probability of occurring are among the lowest energy structures for every value of x .

The key finding from these calculations is that the uranium atoms are distributed throughout the cell and do not form clusters in the lowest energy configurations. This indicates that any stabilisation effects of forming uranium clusters within the ThO₂ matrix are overcome by the likely entropic effects of the less-ordered structures where the U-U distances are maximised.

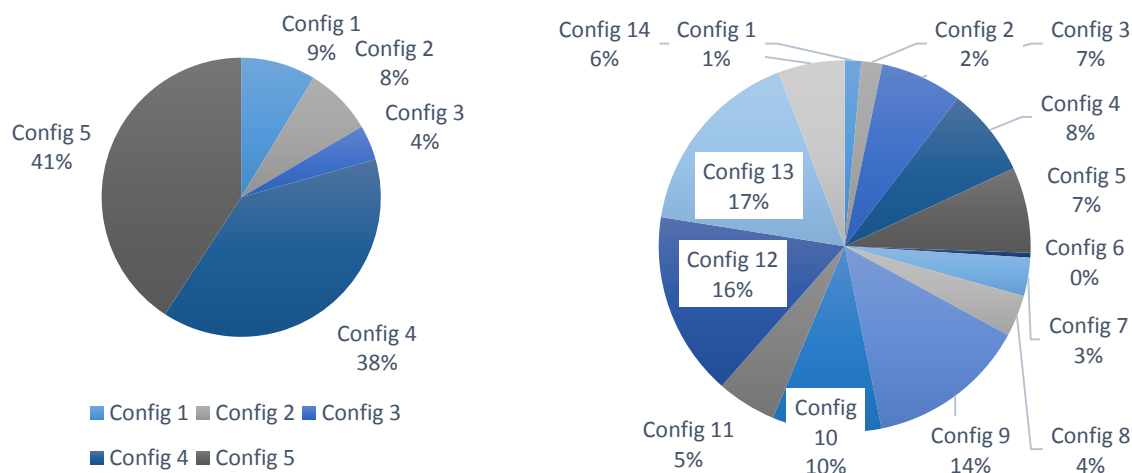


Figure 1. Probability distribution of the independent configurations of $\text{Th}_{30}\text{U}_2\text{O}_{64}$ and $\text{Th}_{29}\text{U}_3\text{O}_{64}$

4. Conclusions:

We have developed a new interatomic potential that can be successfully used in conjunction with a leading UO_2 potential to model uranium-doped ThO_2 . In this study we have applied the potential model to the study the distribution of uranium atoms in thorium supercells. We have shown that uranium atoms do not cluster in the bulk material but are instead distributed throughout the cell.

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