

Derivation of Enhanced Interatomic Potentials for Thorium Dioxide (ThO₂): a Potential Nuclear Fuel

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Abstract

Existing interatomic potentials published for Thorium dioxide have so far been insufficient in modelling all aspects of the material to an acceptable level; some unable to predict the bulk properties or defect properties accurately. A novel method of derivation of interatomic potentials has been employed to calculate a set of potentials that can describe the Thorium-oxygen interaction accurately over the entire region of interest. The potential set will provide an initial platform from which the material can be studied and assessed as to its suitability as an alternative nuclear fuel.

1 Introduction

The use of nuclear power to fulfil the world's energy needs is becoming more popular as the stocks of fossil fuels are quickly depleting; The Nuclear energy institute [1] recorded 30 countries worldwide to be operating nuclear fuel plants in 2012 with 14 countries in potential construction of new power plants. Nuclear power is also considered to be a cleaner energy alternative as no CO₂ gases are released into the environment but in the nuclear fuel cycle other transuranic materials are produced as waste products. Research into the nuclear power industry has been plentiful for many years trying to find ways to improve the current methods.

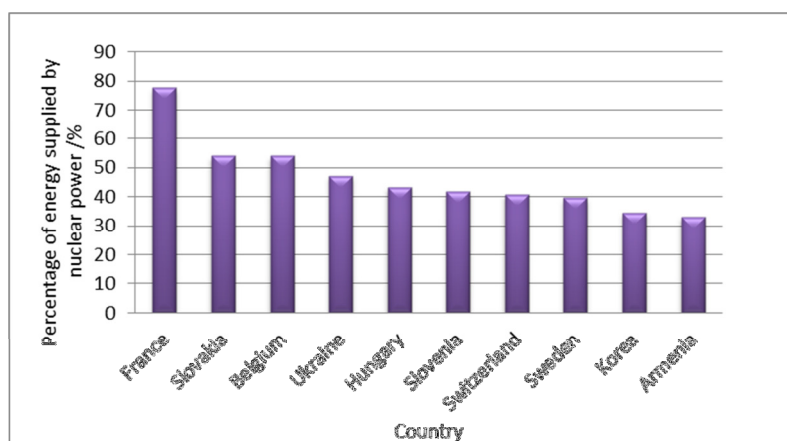


Figure 1.0: Countries that use nuclear power to supply over a quarter or more of their needs using nuclear power (2011). [1]

Uranium and Uranium/Plutonium mixed fuels are currently the most widely used fuels in power stations around the world but as the stores of Uranium are also getting low the research has turned to

new potential fuels. The Uranium/plutonium fuel cycle has provided energy for the world quite sufficiently for many years and therefore finding a material that can replace these fuels must have many benefits; such things as cost, abundance, performance in higher burn up, environmental factors, waste factors and resistance to proliferation.

Thorium dioxide has been investigated and discussed as a potential nuclear fuel for many years [2, 3] and has even been trialled in some countries; India is currently planning on building their first advanced heavy water reactor that will use Thorium as the bulk of the fuel [4].

Thorium is four times more abundant in the earth's crust than uranium and the Thorium process itself has many benefits over the Uranium fuel cycle; it produces much less transuranic waste as less plutonium is produced and the cycle can consume waste plutonium and other actinides. This reduces the problems of waste management and proliferation.

Computational studies of Thorium dioxide have been plentiful along with experimental studies to investigate Thorium dioxide as a nuclear material. Studies include crystal properties such as lattice parameters and lattice energies, elastic properties such as bulk modulus and elastic constants and also studies as to how the material will react under pressure, temperature and radiation using XRD, neutron diffraction and many other techniques.

Published interatomic pair potentials have been reviewed for their sustainability in reproducing both the structural, physical and mechanical properties of thorium dioxide. It is vital that at the computational level the material is modelled correctly so that as the research moves onto experimental all of the predications are correct. Therefore, a set of interatomic potentials has been derived using a novel fitting procedure in order to improve the understanding of ThO₂ and its characteristics.

2 Computational techniques

2.1 Empirical potentials and lattice properties

The general utility lattice program (GULP) [5] was used throughout this investigation to complete all the calculations.

To be able to describe a model accurately all of the interactions between the atoms within the crystal must be considered. The calculations are performed using the Born-model in which the total energy is partitioned into two interactions; the long range and short range interactions. The short range interaction can be represented by the Buckingham equation shown in equation 1.

$$\phi_{(rij)}^{Buckingham} = A_{ij} \exp\left(-\frac{rij}{\rho_{ij}}\right) - C_{ij}r_{ij}^{-6} \quad (1)$$

Where A , ρ and C are the potential parameters that represent the interactions between the atoms i and j and r is that distance between the atoms.

Another form of the Buckingham potentials is used to describe the anion-anion potential used within this investigation. The Buckingham four range (equation 2) form of the potential and it is used to eliminate the unphysical attraction between the ions at close range by applying the potential over specific intervals.

$$V_{\text{Buck-4}}(r_{ij}) = \begin{cases} A_{ij} \exp(-r_{ij}/\rho_{ij}) & \text{if } r_{ij} \leq r_1 \\ \text{5th order polynomial} & \text{if } r_1 < r_{ij} \leq r_{\text{min}} \\ \text{3rd order polynomial} & \text{if } r_{\text{min}} < r_{ij} \leq r_2 \\ -C_{ij}/r_{ij}^6 & \text{if } r_{ij} > r_2 \end{cases} \quad (2)$$

2.2 The shell model

The shell model [6] is applied as it accurately describes the electronic polarization of the model and is beneficial when investigating the defects within a crystal. The shell model describes the interactions in such a way that the ion charge is partitioned between the core and the shell. The core and shell are screened from each other but connected by a harmonic spring with a spring constant (K_2).

2.3 Defect properties

Defect properties of nuclear fuels are very important as they will be subject to both doping and radiation damage. To describe the defect accurately the Mott Littleton approach is used [7]. This model separates the area surrounding the defect into regions in which the outer atoms are contained. The atoms in region 1 are relaxed explicitly as they are the most effected by the defect and the atoms in region 2a are less affected by the defect and can be treated as dielectric continuum in which the ions interact with a net charge from the defect.

3 Discussion of results

The ThO_2 crystal adopts a fluorite structure ($Fm\bar{3}m$) with a lattice constant of 5.6001\AA [8]. The bonding within the system is predominantly ionic with the thorium atoms occupying the face centred position and the oxygen's positioned at the tetrahedral sights.

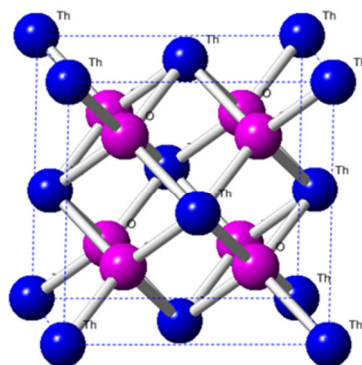


Figure 2.0: Observed crystal structure for ThO_2

3.1 Derivation of interatomic potentials

Bahera *et al.* [9] provide a detailed review of existing Thoria potentials in which they compare the potentials ability to model the bulk properties such as defect properties and surface properties. In order for the potential set to be considered suitable the difference between all predicted properties experimental observation should be as small as possible. Therefore the potential set must be as accurate as possible. In order to derive a suitable set of potentials that are able to model the structure

perfectly a very detailed fitting method must be applied. The method described within this work has been previously successfully used by Read *et al.* [10] to derive a set of potentials to describe UO_2 .

3.1.1 The anion-anion potential

The anion-anion potential used throughout this work is that of Lewis and Catlow [11]. This potential has previously been used successfully in modelling both UO_2 [10] and ThO_2 [12].

Table 1.0: Buckingham four range potential set for the anion-anion interaction.

Interaction	A /eV	$\rho/\text{\AA}$	C /eV \AA^{-6}	Y e	$K_2/\text{eV}\text{\AA}^{-2}$
	11,272.6	0.1363	134.0	-4.4	296.2
O- O	$r_{\min}/\text{\AA}$	Cut 1 / \AA	$r_{\min}/\text{\AA}$	Cut 2 / \AA	$r_{\max}/\text{\AA}$
	0.0	1.2	2.1	2.6	15.0

Where Y is the charge on the ion, K_2 is the spring constant and r_{\max} is the cut-off point.

3.1.2 The cation-anion potential

As the Buckingham four-range potential cannot be applied to the cation-anion potential, due to the absence of a stationary point within the function, the C term must be set to zero so that the unphysical attractive forces at short distances can be avoided. This provides a Born-Mayer form of the potential in which only the A and ρ terms are used to describe the material.

The derivation process begins with the screening of a set of A and ρ values in which a solution set is produced. The solution set will show the combinations of the potentials A and ρ that will give the lattice constant closest to the observed value.

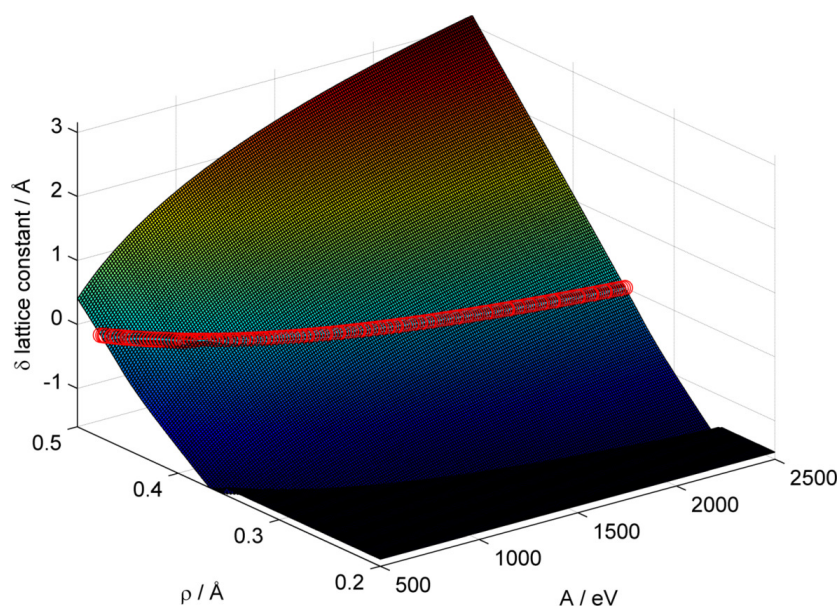


Figure 3.0: Surface plot representing the difference between the A and ρ and the observed Th-O lattice constant.

The solution set is then screened once again to fit to bulk properties. Elastic constants are used as they describe the response of the lattice with respect to deformation of the material. As the material is cubic symmetry reduces the unique elastic constants to C_{11} , C_{12} and C_{44} .

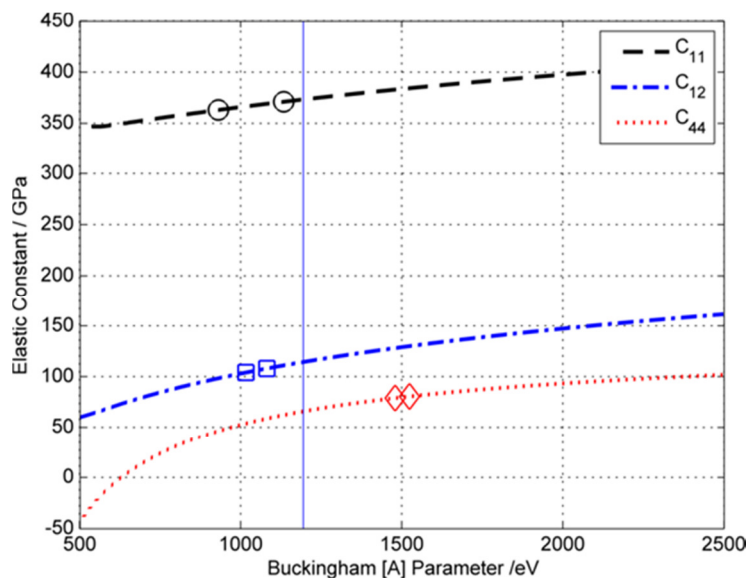


Figure 4 : Predicted and experiental elastic constants plotted against the potential paraeter (A).

Due to the value of C_{44} showing a significant difference in value three approaches were taken to try to fit the elastic constants as best as could be done resulting in three sets of potentials (Shown in table 2.0).

Table 2.0: Three sets of Buckingham potentials for the Cation-anion interaction.

	A / eV	$p / \text{\AA}$	$C / eV\text{\AA}^{-6}$	$Y e $	$K_2 / eV\text{\AA}^{-2}$
Set 1	1394.4724	0.3861	0.00	-2.54	91.9415
Set 2	1047.7387	0.4078	0.00	-2.54	129.5660
Set 3	1193.9986	0.3975	0.00	-2.54	105.7408

Where Y is the charge on the ion and K_2 is the spring constant.

The next step involved adjusting the spring constant to fit the dielectric properties of the material. This is so that the potentials will perform accurately when calculating defect properties within the structure.

Once the spring constant has been adjusted the potential can be initially validated as to its behaviour under varying temperatures by investigating the changes in lattice constant (A) and the lattice energy.

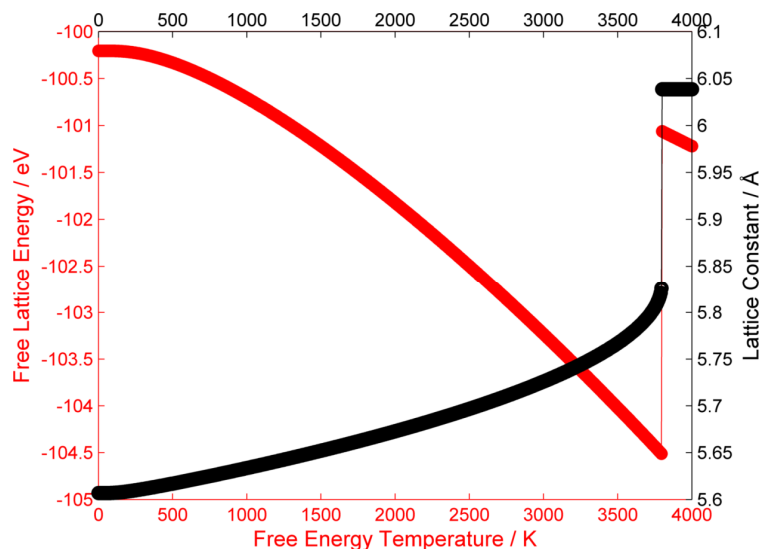


Figure 5: Thermal stability of the potential (set 3)

Investigations into the thermal stability of the potentials conclude that all three of the potential sets are suitable up to 3700K.

3.2 Perfect Lattice properties

The three potentials sets were used to calculate bulk properties of the material including elastic constants, Bulk modulus and dielectric properties. A least squares method was used to determine which potential set was able to reproduce the experimental results the best.

Table 3.0: Born-Mayer potential for the Th-O interaction

Interaction	A / eV	p/Å	C / eVÅ ⁻⁶	Y e	K ₂ / eVÅ ⁻²
Th-O	1193.9986	0.3975	0.0	-6.54	105.7408

The resulting set of potentials is shown in table 3.0 and the bulk properties calculated shown in table 4.0.

Table 4.0: Comparison of calculated and experimental bulk properties

Property	Observed	Calculated	% Difference
Lattice constant (a₀) / Å	5.6001 [8]	5.6001	0
Lattice energy /	-104.39 [13]	-100.33	4.11
Elastic constants /GPa			
C₁₁	367 ± 4.0 [14]	373.23	-1.69
C₁₂	106 ± 2.0 [14]	114.36	-7.92
C₄₄	79.7 ± 0.8 [14]	65.82	17.44
Moduli			
Bulk	193 [14]	200.65	-3.96
Shear	95.6-100.6 [14]	81.93	14.30
Youngs	256,270 [15]	319.58	-24.84
Poissons Ratio	0.279 [14]	0.23	-6.64
Dielectric constants			

Static	18.9 [16]	18.1	4.23
High frequency	4.4 [16]	4.7	-6.82
Phonons at 298K			
L mode	269.2/279 [17,18]	271.37	-0.81
T mode	569.8/567 [17,18]	425.48	25.33

Table 4.0 shows the percentage difference between the observed and calculated bulk properties; the excellent agreement over the range of properties shows that the potential is robust and can be used, with confidence, for further calculations.

3.3 Defect properties

After a robust set of potentials have been determined further investigations can be carried out starting with defect properties. The most basic of defects that can occur within a crystal are point defects. These consist of vacancies and interstitials. The calculated formation energies of these defects within the ThO₂ crystal are listed in Table 5.0.

Table 5.0: Defect formation energies for isolated defects within the ThO₂ unit.

Defect	Published Formation energy /eV [14]	Coordinate position	Calculated Formation energy /eV
Th⁴⁺ vacancy	84.66	(0,0,0)	78.05
O²⁻ vacancy	15.83	(0.25,0.25,0.25)	16.15
Th⁴⁺ Interstitial	-64.86	(0.5,0.5,0.5)	-59.13
O²⁻ Interstitial	-9.82	(0.5,0.5,0.5)	-11.06

3.3.1 Frenkel and Schottky defects

Vacancy and interstitial defects can be combined to calculate the energy of frenkel and schottky defects within a material.

$$Th_{Th}^x \rightleftharpoons V_{Th}'''' + Th_i^{''} \quad (3)$$

$$O_O^x \rightleftharpoons V_O^{\cdot\cdot} + O_i^{''} \quad (4)$$

$$Th_{Th}^x + 2O_O^x \rightleftharpoons V_{Th}'''' + 2V_O^{\cdot\cdot} + ThO_2 \quad (5)$$

Equations 3-5 represent the frenkel (3, 4) and schottky (5) defect calculations.

The results are shown in table 6.0 and they suggest that oxygen frenkel pairs are the most favourable defect to form within the structure.

Table 6.0: Frenkel and Schottky energies within the ThO₂ cell (per defect).

Defect	Experimental formation energy /eV	Calculated formation energy /eV
Th Frenkel	19.8	18.916
O Frenkel	6.01	5.092
Schottky trio	11.93	10.020

4. Conclusions

A potential set has been derived using available experimental data and a novel method of potential fitting. The potentials were then tested as to their ability to reproduce bulk properties and defect properties of the material.

The potentials showed a very good agreement with experimental data with little percentage difference. The defect calculations also showed good agreement with previously published data and the calculations also showed that oxygen frenkel pairs were the most favourable defect to form.

5. Acknowledgements

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6. References

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