**The 8th Pacific Rim International Congress on Advanced Materials and Processing**
*Edited by: Fernand Marquis*
***TMS (The Minerals, Metals & Materials Society), 2013***

# FIRST PRINCIPLES STUDIES OF MECHANICAL PROPERTIES OF THORIA

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Keywords: Thoria, First Principles Studies, Mechanical Properties

## Abstract

Thoria-based fuel is regarded as a fuel for safer nuclear reactors as it has higher thermal conductivity and melting point than urania, which prevents reactor melt down. Although thoria fuel has been investigated additional studies of its properties are required. In particular available experimental data are scattered. First principles methods were used to predict correctly that thoria is an insulator. The calculated band gap of thoria by local functionals (LDA and generalized gradient approximation, GGA): has a value 4.4-4.5 eV; for LDA + U (6 eV) the band gap is 4.7 eV). Nonlocal B3LYP functional gives a larger band gap (6.9 eV), in better agreement with the experiment (6 eV). The calculated elastic moduli using new GGA and B3LYP are in good agreement with LDA calculation, while PBE and LDA+U results are slightly lower than most experimental values. In general the results obtained are in agreement with reliable experimental data.

## Introduction

At the time of increasing cost of traditional urania fuel, it is more economically justified to look at the alternative fuels like thoria [1]. Thoria is also regarded as a fuel for safer reactors as it has a higher thermal conductivity (for most temperatures of interest) and melting point [1] than urania, which prevents reactor melt down.

The following paper discusses the application of *Density Functional Theory (DFT)* to assess the mechanical and structural properties of thoria fuel. Detailed calculations of the crystal structure and mechanical properties of new fuel materials complement experimental measurements, and they enhance our understanding of the structural properties of fuel used in nuclear reactors.

The CASTEP quantum mechanical code, employing density functional theory [2], is commonly used to study the structure and properties of materials. The CASTEP code uses pseudopotentials and it has already been demonstrated [3] that plane wave ultrasoft pseudopotentials predict structural properties that are very close to experimental values for various compounds containing lanthanides and actinides.

Using the total energy minimization method [2], the equilibrium lattice constants and the positions of atoms of thoria can be calculated. The current calculations were performed for temperatures of 0 K and for idealized structures with small unit cells. Such small unit cells are convenient to use in *first-principles* methods simulations, since the demand on computational resources is reduced.

The structural optimization according to the Broyden–Fletcher–Goldfarb–Shanno (BFGS) of the total energy minimization is used [2]. This minimization is performed using iterative methods; when forces and stresses are minimized (almost vanish), the equilibrium lattice

constant and the positions of atoms of stoichiometric thoria are calculated. The calculated lattice constants of $ThO_2$ using this procedure agree with the experimental data.

The elastic constant calculations are presented for single crystals of $ThO_2$. The experimental values of shear (G) and Young (Y) moduli pertain to a grain aggregate where grains have randomly orientated crystallographic directions, and this assumption applies to the calculation of the respective moduli.

**Structure of thoria**

The CASTEP *first-principles* calculations of lattice constants of thoria were presented in reference [4] although the Generalized Gradient Approximation (GGA) framework [5,6] was not used since the early GGA implementation lead to significantly overestimated bond length and underestimated bulk moduli [7,8]. However, GGA is widely used to correct significantly underestimated lattice constants by LDA. The presented here results demonstrate that the more recently proposed GGA: Wu-Cohen functional (WC) [9], Perdew-Burke-Ernzerhof version that improves equilibrium properties of densely packed solids and their surfaces(PBEsol) [10] leads to improved lattice constant values with bulk (B) modulus in agreement with experiment (Section 3).

The structure of thoria is shown in Fig. 1.

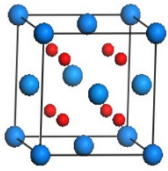

Figure 1: Lattice structure of thoria. Thorium and oxygen atoms are marked as spheres, with the larger radius of Th than O atoms.

In Table I we present for comparison our previous calculations of the lattice constant of thoria [4] using LDA [11] and LDA + *U* [12] with ultrasoft potentials (USP, OTFG) [13] and the calculations using nonlocal the B3LYP functional [14] using norm-conserved potentials (NCP) in the Kleinman-Bylander form (optimized with respect to the cutoff energy [15]).

The agreement with the experimentally measured lattice constants: 0.5598 nm [16] and 0.5600 nm [17] are in good agreement with calculations (Table I) when correction (for thermal expansion) by about 0.002 nm is taken into account with the exception of LDA, which predicts slightly smaller value (0.553 nm). As expected, within GGA scheme increased values are found (0.555 nm (PBEsol) and 0.556 nm (WC)) in good agreement with experiment while PBE leads to slightly over- predicting value (0.561 nm).

In Fig. 2 the predicted within LDA, WC and B3LYP functional densities of states of thoria are shown and we found that all GGA and LDA predict almost identical density of states with underestimated band gap as shown in Table I (WC band gap 4.445 eV, PBE: 4.493 eV, PBEsol: 4.448 eV and LDA 4.511 eV versus experimental: 6 eV [18]). Only B3LYP functional leads to a larger band gap (6.895 eV), in better agreement with experiment).

**Table I** Lattice constants, spins, electronic charges (on oxygen atoms), band gaps and energies (per non-oxygen atom) calculated using CASTEP [2].

| Compound | Structure | Energy per non-O atom [eV] | Method | Lattice constants (*a*) [nm] | Charge on oxygen atom [electron] (Mulliken) | Band gap Width eVs |
|---|---|---|---|---|---|---|
| $ThO_2$ | $Fm\bar{3}m$ | -31.73 | LDA (USP) | 0.553 | -0.69 | 4.511 |
| $ThO_2$ | $Fm\bar{3}m$ | -31.09 | PBE (OTFG) | 0.561 | -0.73 | 4.493 |
| $ThO_2$ | $Fm\bar{3}m$ | -32.43 | PBEsol (OTFG) | 0.555 | -0.69 | 4.448 |
| $ThO_2$ | $Fm\bar{3}m$ | -41.5 | WC (OTFG) | 0.556 | -0.72 | 4.445 |
| $ThO_2$ | $Fm\bar{3}m$ | -24.57 | LDA+ *U* (6 eV) (USP) | 0.555 | -0.71 | 4.700 |
| $ThO_2$ | $Fm\bar{3}m$ | -33.98 | Hybrid (B3LYP) (NCP) | 0.559 | -0.87 | 6.895 |
| $ThO_2$ Experiment | $Fm\bar{3}m$ | | | 0.5598 [16] 0.5600 [17] | | ~6 [18] |

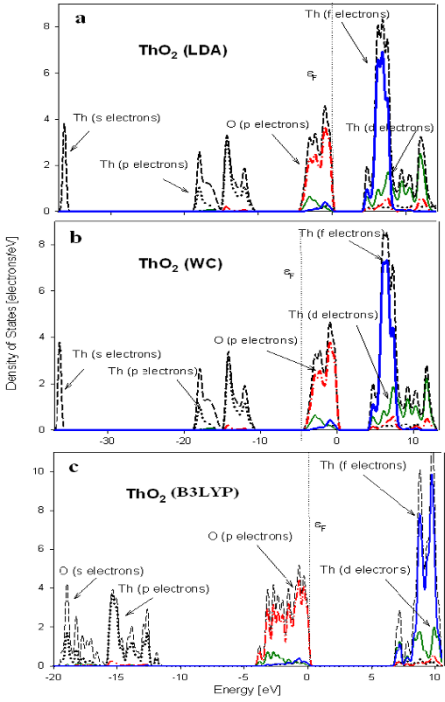


Figure 2**.** The calculated total (black, dashed line) electron density of states of thoria using LDA, WC and B3LYP functional. The projected density of states of 2p electrons of oxygen is indicated by a red dot-dashed line, while 5f electrons of thorium are indicated by a blue solid line. Additionally, 6d and 6 p electrons on thorium are indicated by a thin, green solid line and dotted black line, respectively. The main character of electrons at various energies is labeled with arrows.

## Elastic properties of thoria

The experimental values of elastic moduli pertain to a grain aggregate (where grains have randomly orientated crystallographic directions) rather than to single crystals. A completely random orientation of the grains is assumed in the computation of share and young modulus.

**Table II** Elastic Properties of thoria, calculated using LDA [11], GGA: (PBE [6], PBEsol [10], WC [9] and LDA+U [12] and non-local functional (B3LYP [14]) as indicated.

| Property (in GPa; # unit-less) | $ThO_2$ (LDA) | $ThO_2$ (PBE) OTFG USP [14 A] | $ThO_2$ (PBEsol) OTFG | $ThO_2$ (WC) OTFG | $ThO_2$ (Hybrid) (B3LYP) (NCP) | $ThO_2$ (LDA + $U$) ($U$ = 6 eV) (USP) | $ThO_2$ Experiment (fully dense) |
|---|---|---|---|---|---|---|---|
| $B$ | 213.4 | 187.6 | 202.8 | 203.0 | 196.2 | 173.0 | 193 [19,20] 223 [21] |
| $G$ | 102.2 | 85.4 | 96.6 | 96.4 | 106.8 ($G_V$) | 100.3 | 100.1, 100.8 [22] 97.2 [19] |
| #$G/B$ | 0.48 | 0.46 | 0.48 | 0.47 | 0.54 ($G_V/B_V$) | 0.58 | $G/B_{average}$ 0.48 |
| $Y$ ($Y_{(x,y),}$ $Y_{(z)}$) | 264.4 (321.5) | 222.4 (303.4) | 250.1 (313.3) | 249.7 (312.5) | 271.2 | 252.3 (298.3) | 262.1, 260.6 [22] 247.7 [19] |
| $c_{11}$ | 385.0 ( ± 1.2) | 351.9 ( ± 2.1) | 370.9 ( ± 1.9) | 370.6 ( ± 1.2) | 373.1 | 337.0 ( ± 2.6) | 377 [21] 367 [20] |
| $c_{12}$ | 127.6 ( ± 0.7) | 105.4 ( ± 1.4) | 118.7 ( ± 1.4) | 119.3 ( ± 0.8) | 107.8 | 91.1 ( ± 1.4) | 146 [21] 106 [20] |
| $c_{44}$ | 87.5 ( ± 0.3) | 70.9 ( ± 0.4) | 80.8 ( ± 0.3) | 80.7 ( ± 0.3) | 89.5 | 87.6 ( ± 1.4) | 89 [21] 79 [20] |
| $n$ | 0.25 | 0.23 | 0.24 | 0.24 | | 0.2 | 0.301 [22] 0.284 [19] |

Table II demonstrates that the mechanical moduli calculated using WC and PBEsol are in much better agreement with experimental result [19] of $ThO_2$ than PBE and similarly to LDA and B3LYP lead to higher values of elastic moduli than PBE.

The intrinsic brittleness ($G/B$) [23] does not show much variation within GGA and LDA scheme while B3LYP and LDA+U predict thoria to be more brittle.

## Conclusion

Detailed DFT calculations of the crystal structure and mechanical properties of thoria complement experimental measurements, and they enhance understanding of the properties of fuel used in nuclear reactors. Since there are no fitting parameters in these calculations they can also be used to predict the properties of other novel complex fuels and in particular can become an important tool for modeling the properties of recycled fuels.

## Acknowledgement

The access to high performance supercomputers at CLUMEQ and Westgrid is acknowledged. The authors are grateful to Ki-Seob Sim**,**Victor Milman and Alexander Goldberg for their fruitful discussions and advices.

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