Investigation of ThO_2-based Fuels Using Atomic Level Simulations

Rakesh K. Behera[1], and Chaitanya S. Deo[1]

[1]Nuclear and Radiological Engineering Program, George W. Woodruff School of Mechanical Engineering, Georgia Institute of Technology, Atlanta, GA 30332

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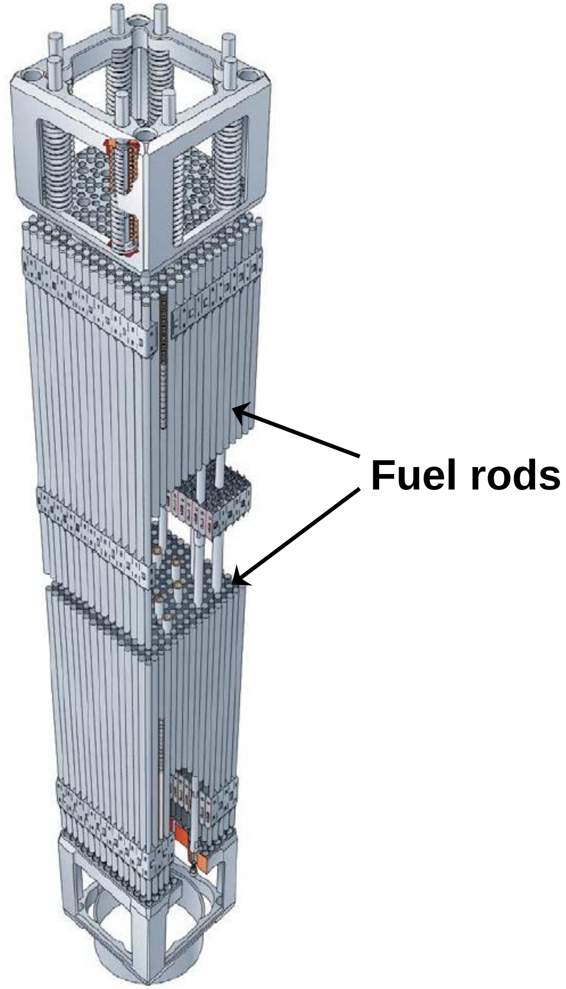
Overview

- UO_2 is the most common fuel used in commercial nuclear reactors
- Advantages
  - High melting point
  - Good temperature-stability
  - Good chemical compatibility with cladding and coolant
  - Resistance to radiation
- Disadvantages
  - Generation of minor actinides
  - Low thermal conductivity
  - Proliferation issue
- ThO_2-based fuels complement uranium fuels and ensure long term sustainability of nuclear power



Schematic of Westinghouse PWR fuel

http://www.westinghousenuclear.com/

Fuel Comparison

	Uranium-based	Thorium-based
Availability	U - 1.7 ppm	Th – 5.8 ppm
Fertile material	^{238}U	^{232}Th
Principal fissile actinide product	^{239}Pu	^{233}U
Melting point	~2800°C	~3350°C
Absorption cross-section for thermal neutrons	^{238}U (2.7 barns)	^{232}Th (7.4 barns)
Oxidation states	U: +4, +6	Th: +4
Thermal conductivity and Radiation resistance	higher than UO_2	
Generation of Pu and long-lived minor actinides (Np, Am and Cm)	lower than UO_2	
Proliferation-resistance	better than UO_2	

US Bureau of Mines, 1975
Belle *et al.*, USDOE, DOE/NE-0060 (1984)
IAEA-TECDOC-1450 International Atomic Energy Agency, (May 2005)

Objectives

- One of the major challenges of thoria-based fuels is
  - The information available on ThO_2 and thoria-based (ThO_2–UO_2) fuels is not as comprehensive compared to UO_2

- **Objectives:** To investigate the properties of ThO_2 and ThO_2–UO_2 mixed-oxide system
  - Elastic properties
  - Phase stability
  - Defect energetics
  - Surface stability
  - Thermal properties

- **Approach:** To characterize the properties using atomic level simulations
  - Molecular Dynamics

Simulation Method

- **Molecular Dynamics (MD)**
  - Each atom is described as a core for rigid ion model (core and shell for shell model)
  - The motion of atoms are guided by the Newton's equation of motion
  - Inputs:
    - Structure
    - Conditions for simulation (temperature, pressure, ensembles, etc.)
    - Atomic interactions (potentials)

- Potentials
  - Long-range: Coulombic interactions
  - Short-range:
    - Buckingham $$V_{buck}(r)=\left[a_{ij}\exp\left(-r/\rho_{ij}\right)-c_{ij}/r^{6}\right]$$
    - Morse $$V_{morse}(r)=D_{ij}\left\{\left[1-\exp\left(\beta_{ij}\left(r-r_{ij}^{*}\right)\right)\right]^{2}-1\right\}$$
    - Core-shell $$V_{cs}(\omega)=\frac{1}{2}k\omega^{2}$$

Interatomic Potentials

- There are only two different interatomic potentials available in the literature to describe ThO_2 (compared to > 20 potentials for UO_2)

- In this study we have developed a few more interatomic interactions

UO_2 pair interactions	U-U	U-O	O-O
ThO_2 pair interactions	Th-Th	Th-O	O-O

- **Approach:** Develop ThO_2 potentials based on the UO_2 interactions

- **Fitting Scheme:** We have used a least-square method available in the General Utility Lattice Program (GULP) to fit the interatomic interactions
  - Fitting parameters:
    - Elastic constants (C_{11}, C_{12}, C_{44})
    - Dielectric constants

Summary of ThO_2 Potentials

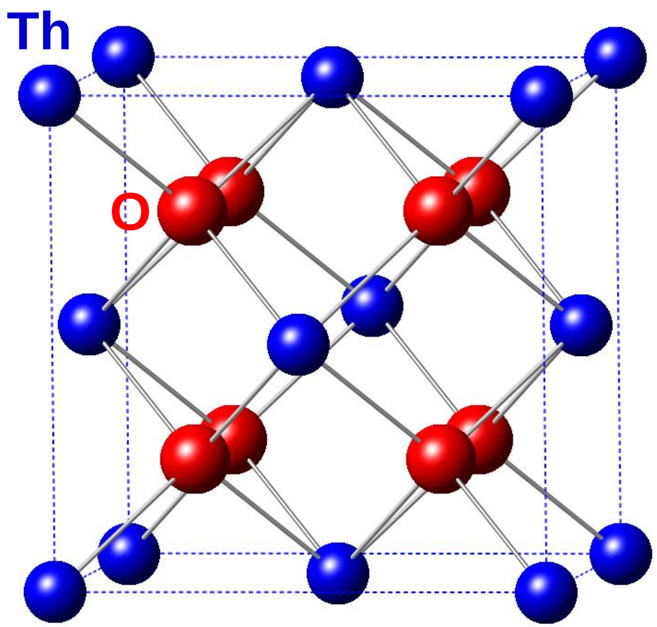
- Following is a summary of all the four pair potentials considered for predicting the properties of thoria

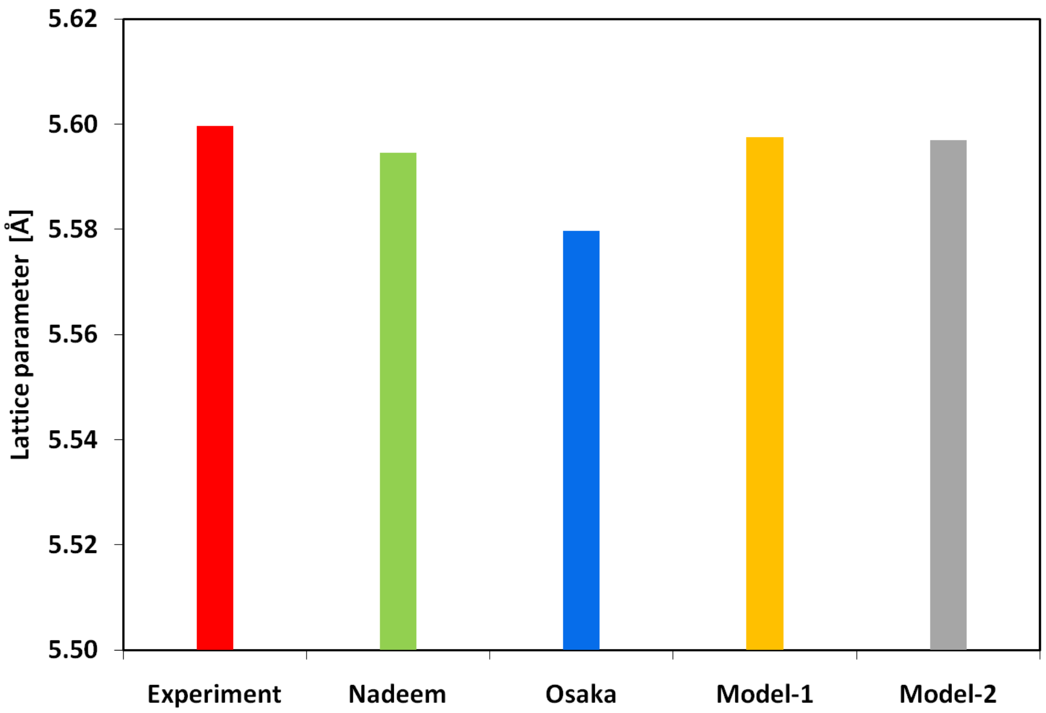
		Referred as
From literature	Nadeem *et al.*	Nadeem
	Osaka *et al.*	Osaka
Fitted (Based on UO_2 models)	Basak *et al.*	Model-1
	Lewis *et al.*	Model-2

- The predicted properties from all the four potentials are compared with available experimental and first-principles calculations

Nadeem *et al.*, J. Mater. Sci. Technol., 17 (2001) 638
Osaka *et al.*, J. Nucl. Sci. Technol., 44 (2007) 1543
Basak *et al.*, J. Alloy. Compd., 360 (2003) 210
Lewis *et al.*, J. Phys. C Solid State Phys., 18 (1985) 1149

1. Lattice Parameter



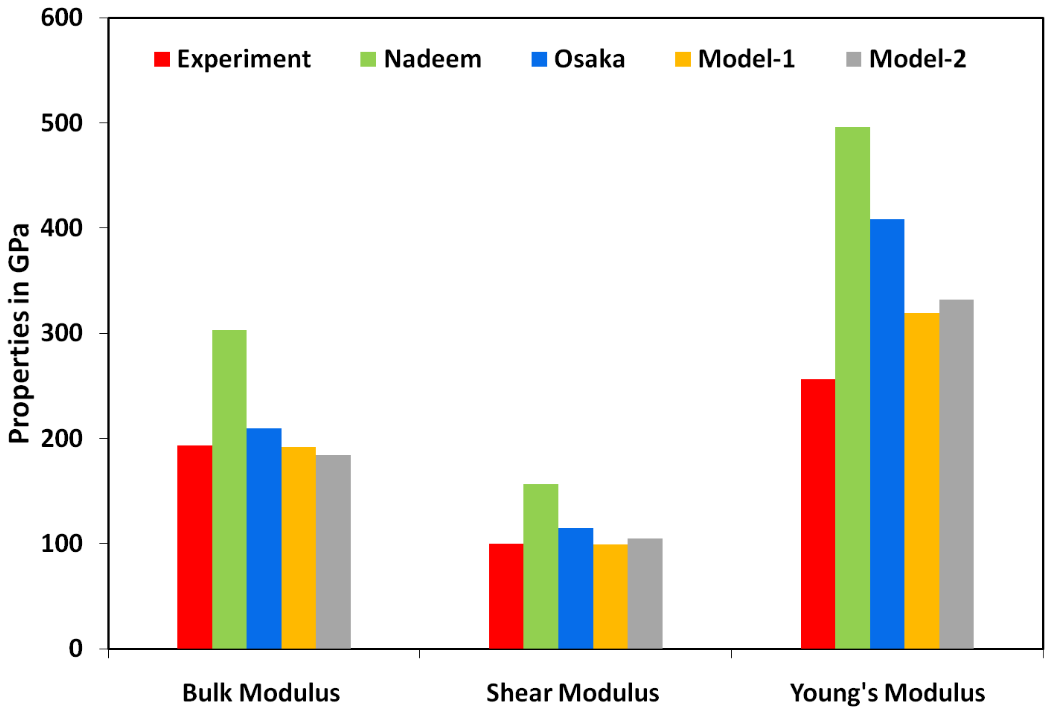


- The lattice parameter calculated for ThO_2 by Model-1 and Model-2 are well compared with the experimental value (< 0.01% deviation)
- Osaka potential underestimated the lattice parameter by ~0.3%

R W G Wyckoff, Crystal Structures, 2nd Ed. (Interscience, New York), 1963

2. Elastic Properties

- Elastic properties, especially elastic constants provide critical information about solids
  - Mechanical stability
  - Stiffness
  - Debye temperature



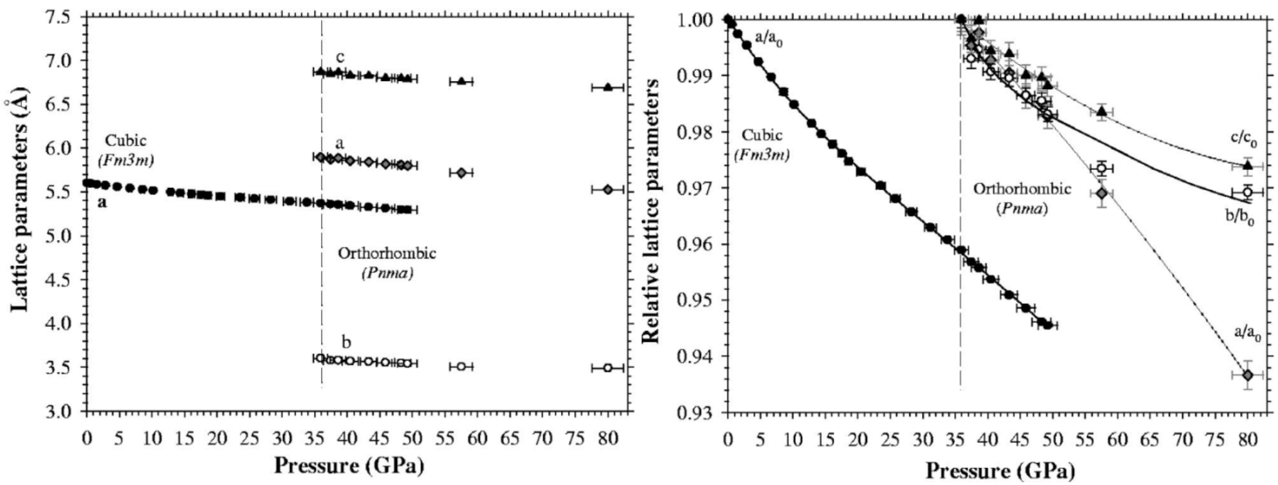
- Nadeem and Osaka potentials overestimated all the modulus values

- Model-1 and Model-2 predicted bulk and shear modulus within 5% of the experimental values, while overestimated the Young’s modulus by ~30%

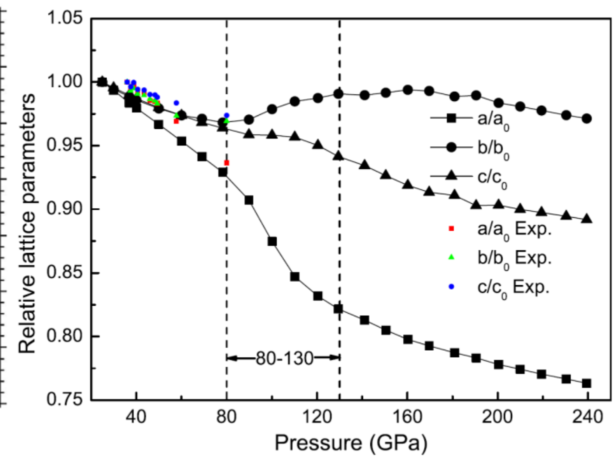
Macedo *et al.*, J. Am. Ceram. Soc., 47 (1964) 651

3. Phase Stability

- The effect of pressure on the phase transition in ThO_2 have been studied with both experiment and first principles calculations



Experiment (Idiri *et al.*)



First principles (Wang *et al.*)

- Similar phase transition is also reported for UO_2 by Idiri *et al.* (Fluorite → Cotunnite)

- Therefore, it is important to analyze the phase stability predicted by each potential for ThO_2

Idiri *et al.*, Phys. Rev. B, 70 (2004) 014113
Wang *et al.*, J. Nucl. Mater., 399 (2010) 181

AO_2 Phases

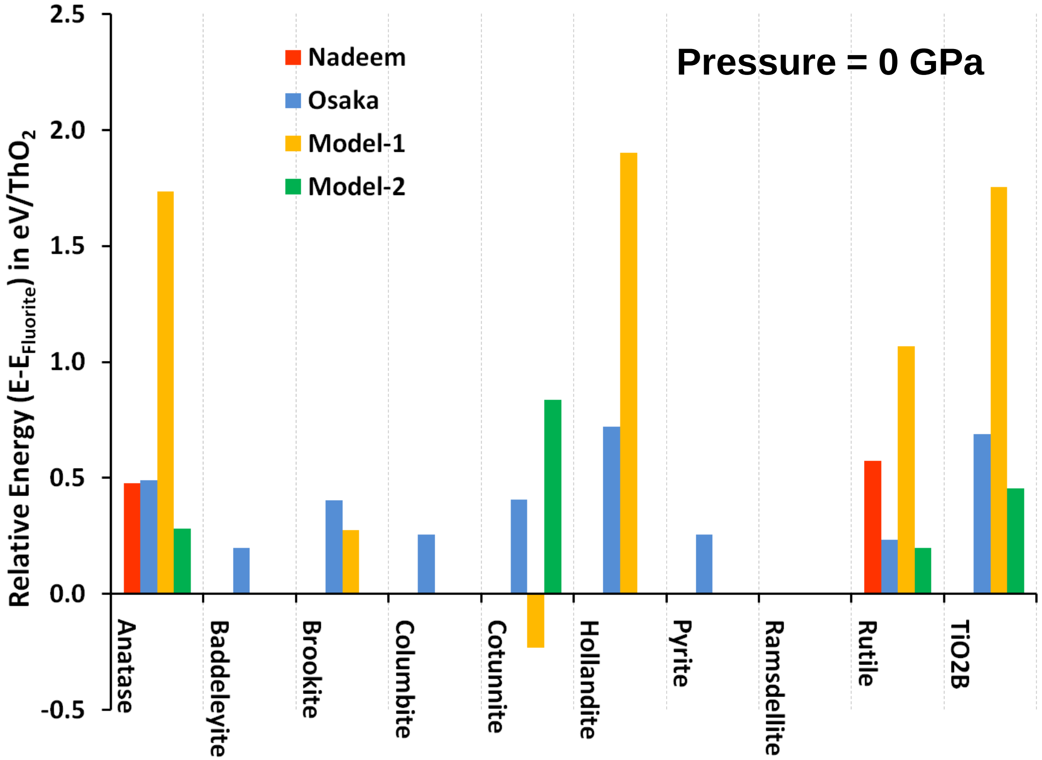
- Following the work by Swamy *et al.* for TiO_2, we have calculated the energies of 11 different AO_2 phases

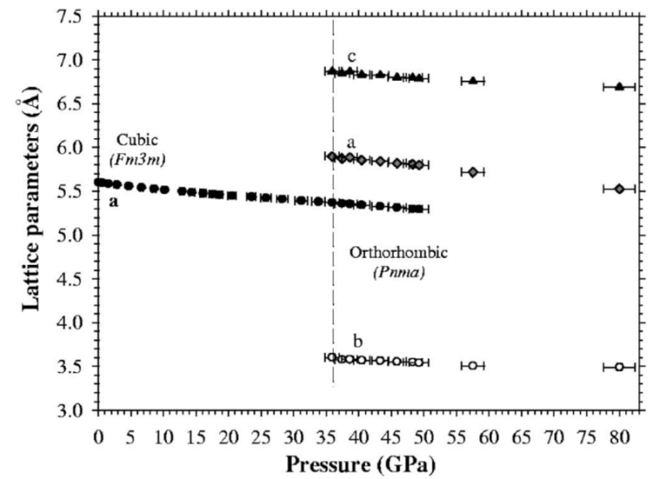
AO_2 phases considered	
Anatase	Hollandite
Baddeleyite	Pyrite
Brookite	Ramsdeleyite
Columbite	Rutile
Cotunnite	TiO_2B
Fluorite	

- Energy of each phase relative to the Fluorite phase is calculated
  - Positive energy: Fluorite phase is energetically more favorable
  - Negative energy: Fluorite phase is energetically less favorable

Swamy *et al.*, J. Phys. Chem. Solids, 62 (2001) 887

ThO_2 Polymorphs





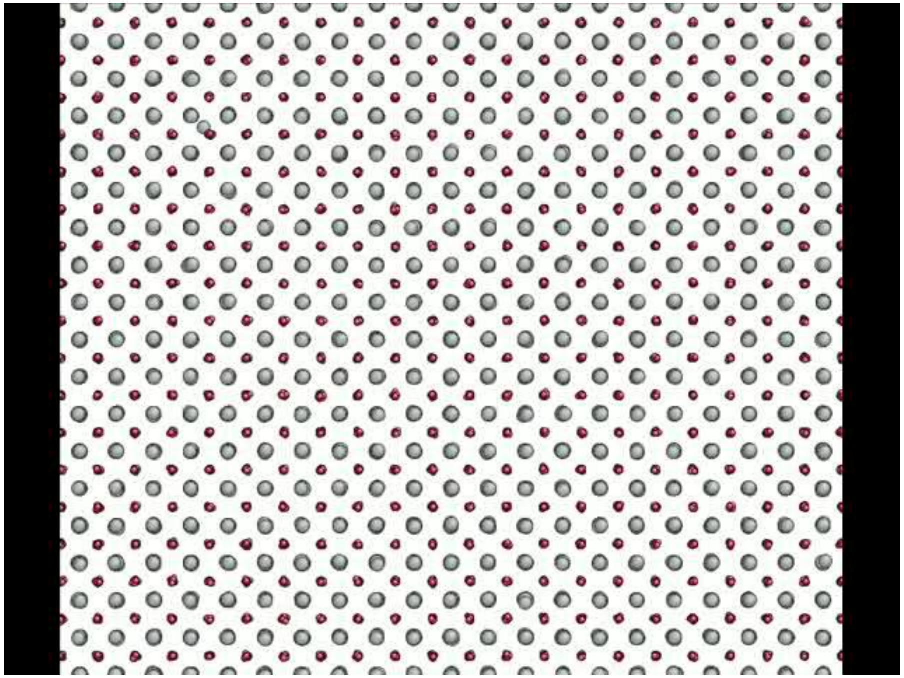
Experiment

- Most of the potentials predicted the Fluorite phase to be energetically favorable compared to the other AO_2 polymorphs
- Model-1 based on the Basak potential predicted Cotunnite phase to be more favorable

Idiri *et al.*, Phys. Rev. B, 70 (2004) 014113

4. Defects in Nuclear Fuel

- The irradiation process, where high-energy particles cause damage to the host lattice, generates a lot of point defects

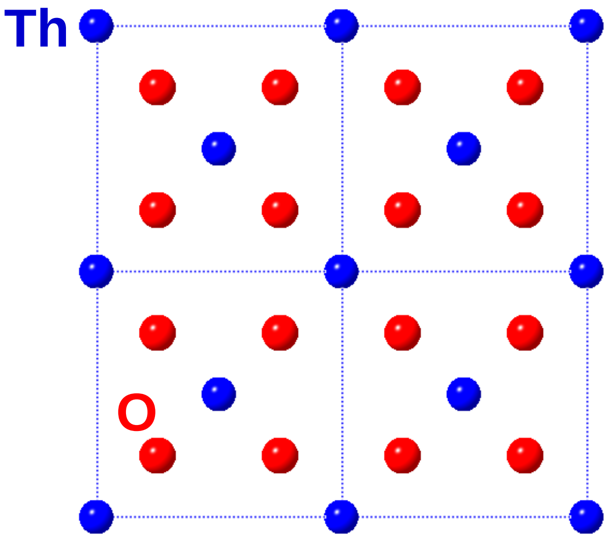


UO_2 lattice
Grey: U-atoms
Red: O-atoms
PKA – U (1 KeV)

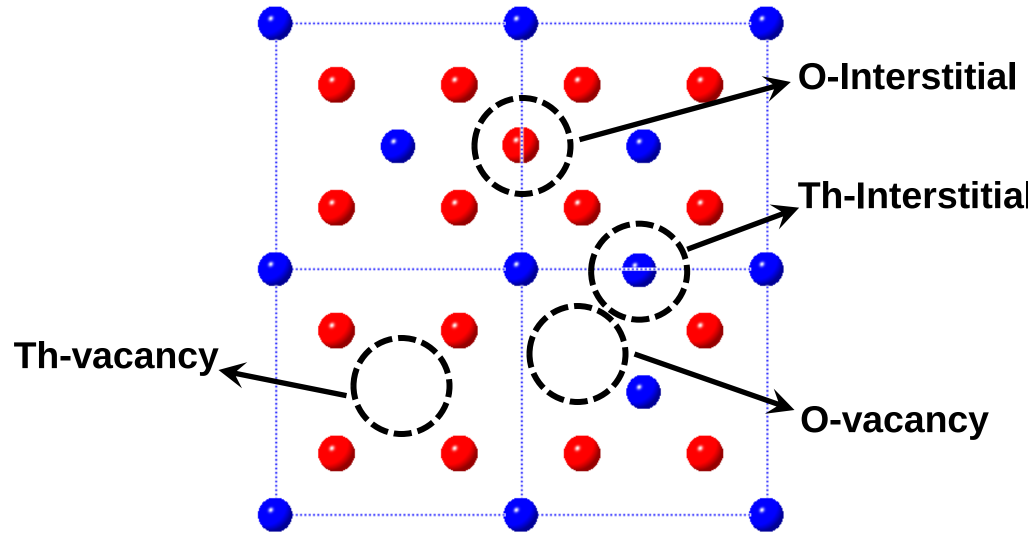
- These defects can influence a range of properties
  - Radiation tolerance
  - Thermal conductivity
  - Fission product accommodation
  - Microstructural evolution

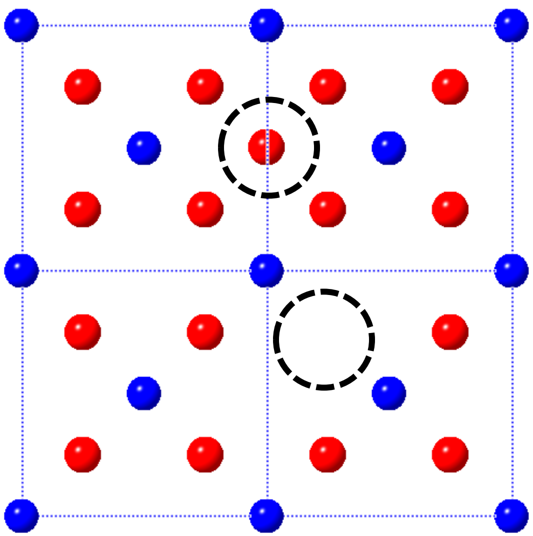
Courtsey: Dr. Dilpuneet S. Aidhy, Argonne National Lab.

Point Defects

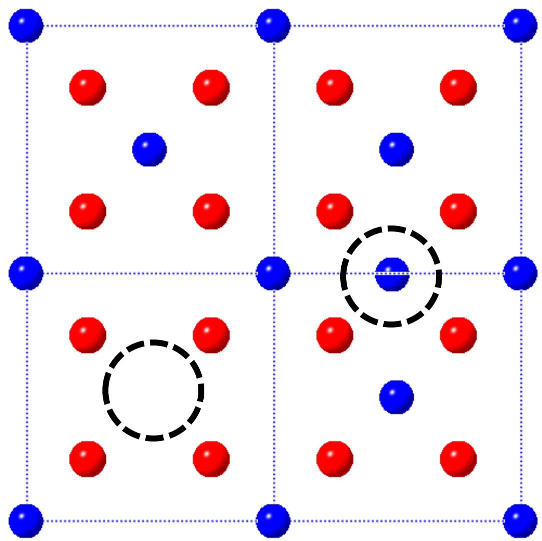


Perfect Lattice

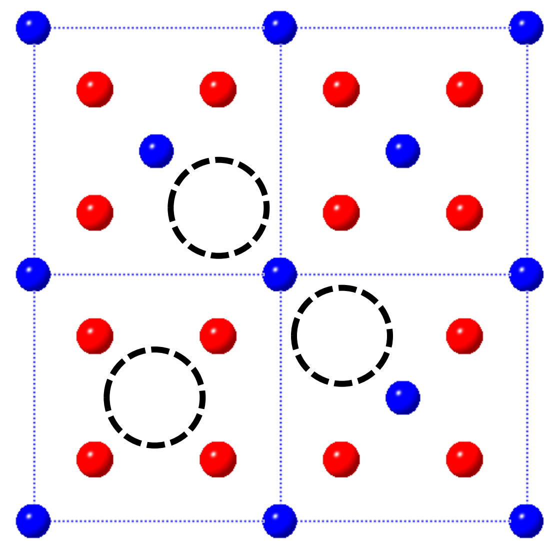




O-Frenkel

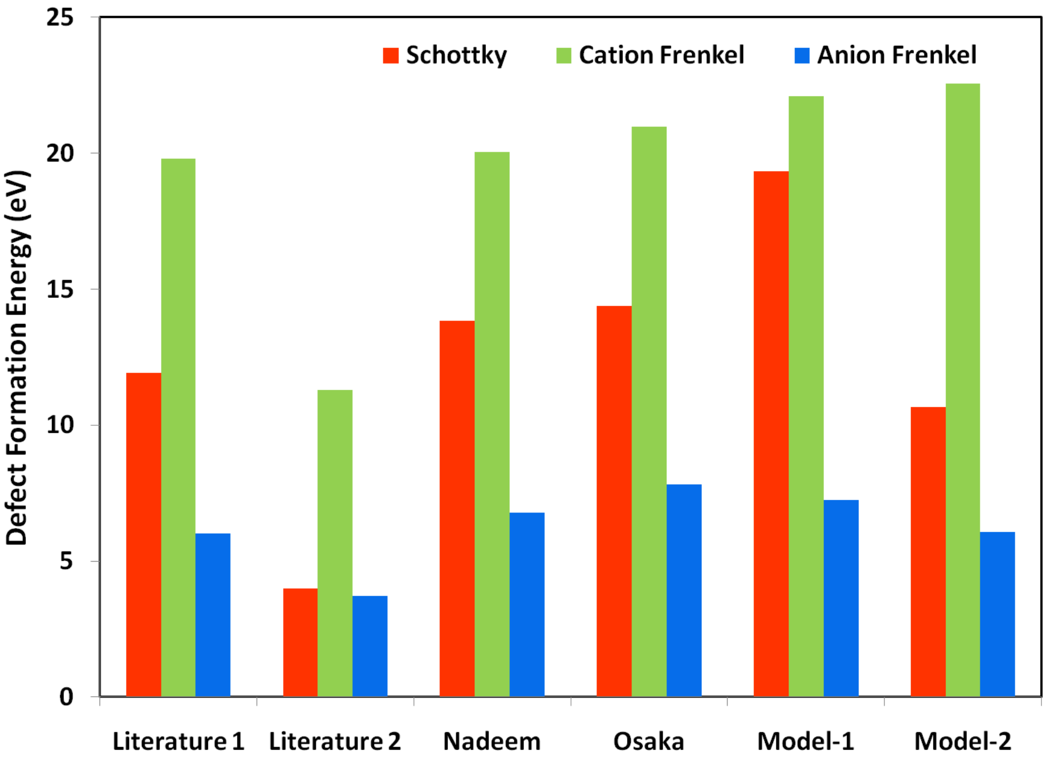


Th-Frenkel



Schottky

Defect Complexes



Literature 1
Colbourn *et al.*, J. Nucl. Mater., 118 (1983) 50

Literature 2
Nadeem *et al.*, J. Mater. Sci. Technol., 17 (2001) 638

Defect formation energy (eV)	UO_2 (Expt.)
Schottky	6.0 – 7.0
Cation Frenkel	9.5
Anion Frenkel	3.0 – 4.6

- The energetics indicated that Anion Frenkel will be the most favorable defect complex in the ThO_2 system

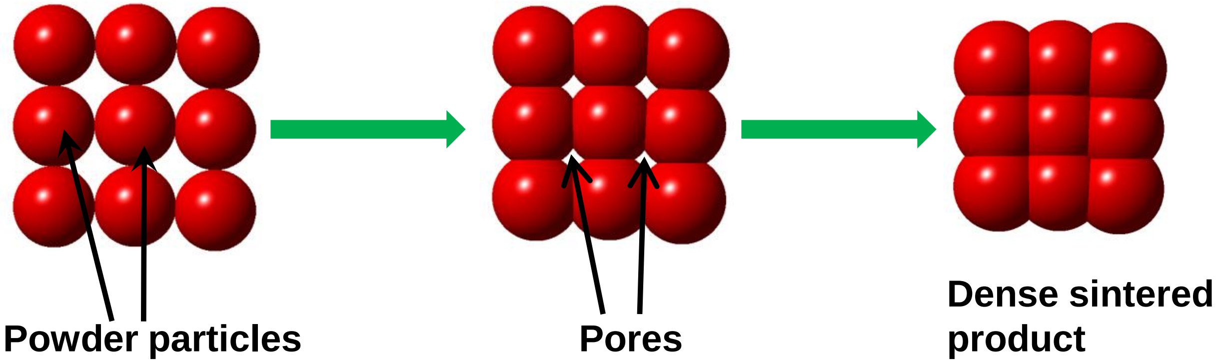
- These results agree well with the literature values as well as stability of defect complexes in UO_2

Matzke H., J. Chem. Soc., Faraday Trans. 2, 83 (1987) 1121

5. ThO_2 Surfaces

- Sintering is a necessary step to form dense ThO_2 pellets from powders

- The reduction of surface energy of the particles is the driving force for sintering. Hence, surfaces play an important role



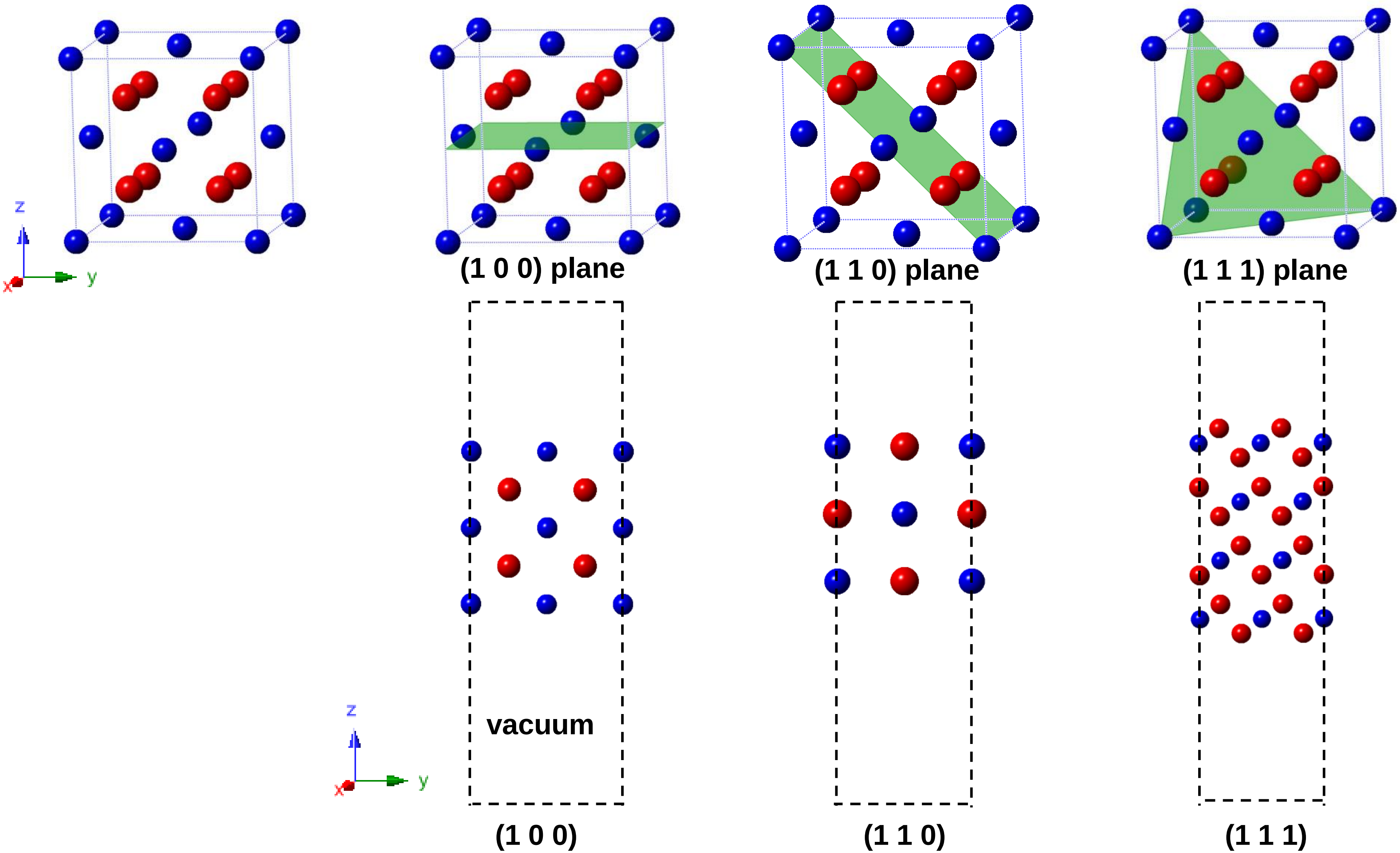
ThO_2 pellets
http://www.dae.gov.in/ar2001/barc.htm

- Since the melting point of ThO_2 (~3350°C) is relatively higher than UO_2 (~2800°C) , it is essential to characterize the surface stability

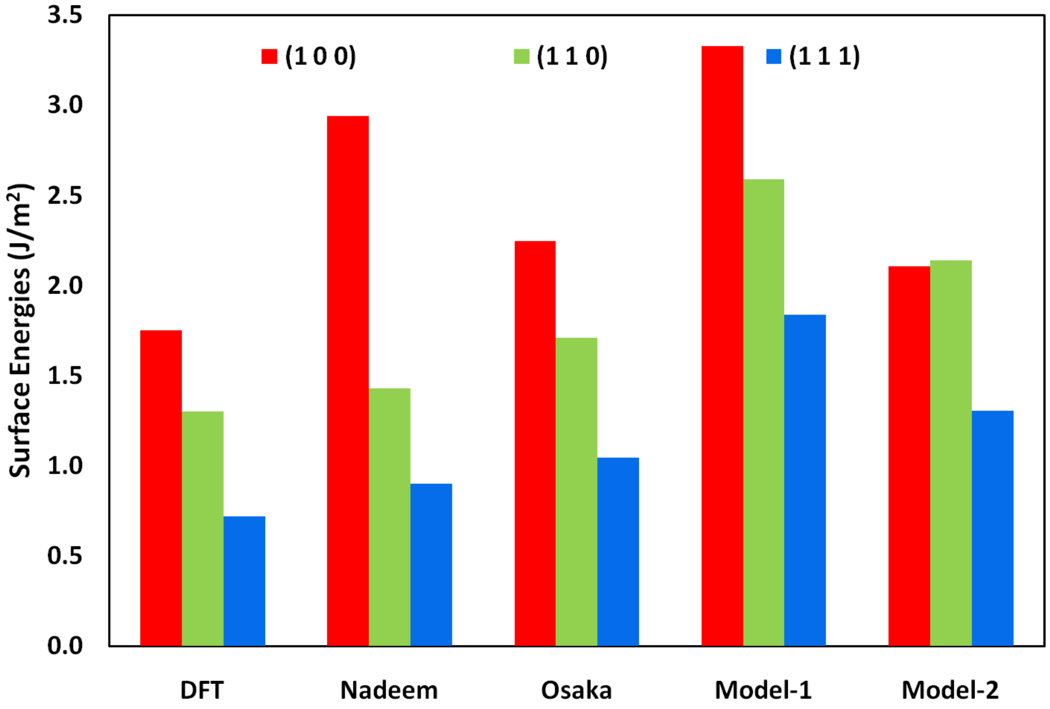
- In addition, the release of fission products can be influenced (either inhibited or enhanced) by specific arrangements of the surface ions

Low-index Surfaces

- The low-index surfaces are the extensively studied surfaces



Surfaces



Surface Energies (J/m^2)	ThO_2 (DFT)	UO_2 (DFT)
(1 0 0)	1.75	1.07
(1 1 0)	1.30	0.83
(1 1 1)	0.72	0.33

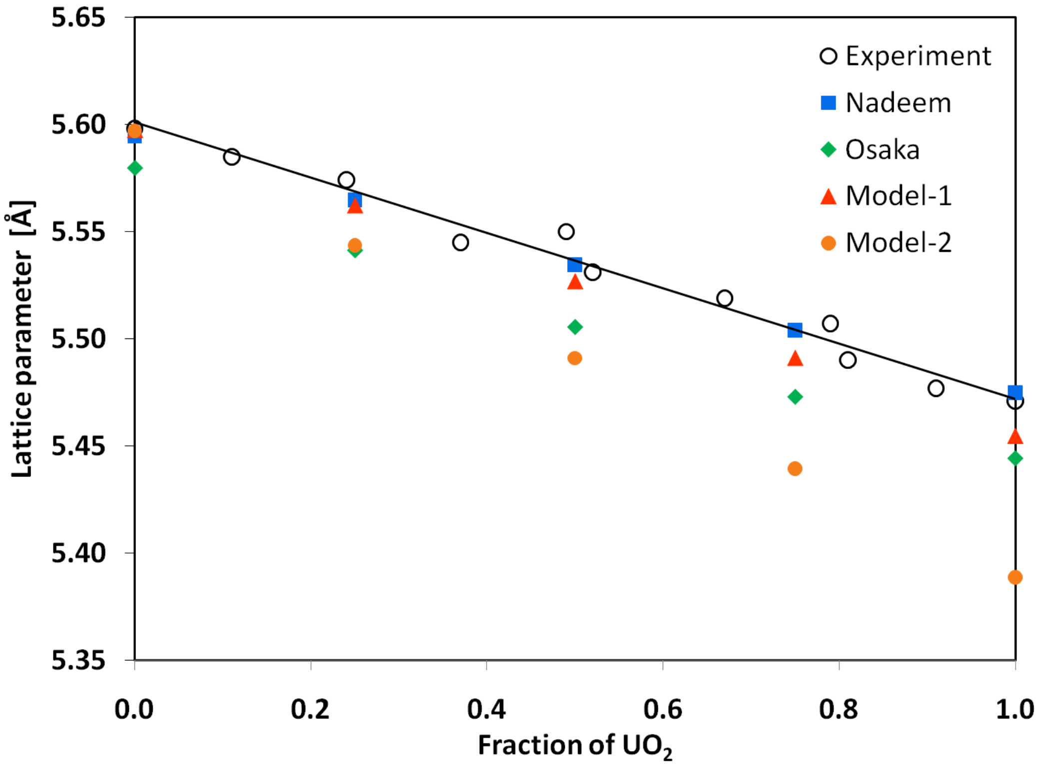
- The predicted results indicate (1 1 1) surfaces to be more stable compared to (1 0 0) and (1 1 0) surface, which is in agreement with first principles calculations

- Similar trend in surface energy is observed for UO_2

DFT - Skomurski *et al.*, J. Nucl. Mater., 375 (2008) 290

6. Mixed Oxide System

- With the overall goal of predicting the mixed ThO_2–UO_2 system, we have analyzed the variation in lattice constant with fraction of UO_2 in the ThO_2 matrix



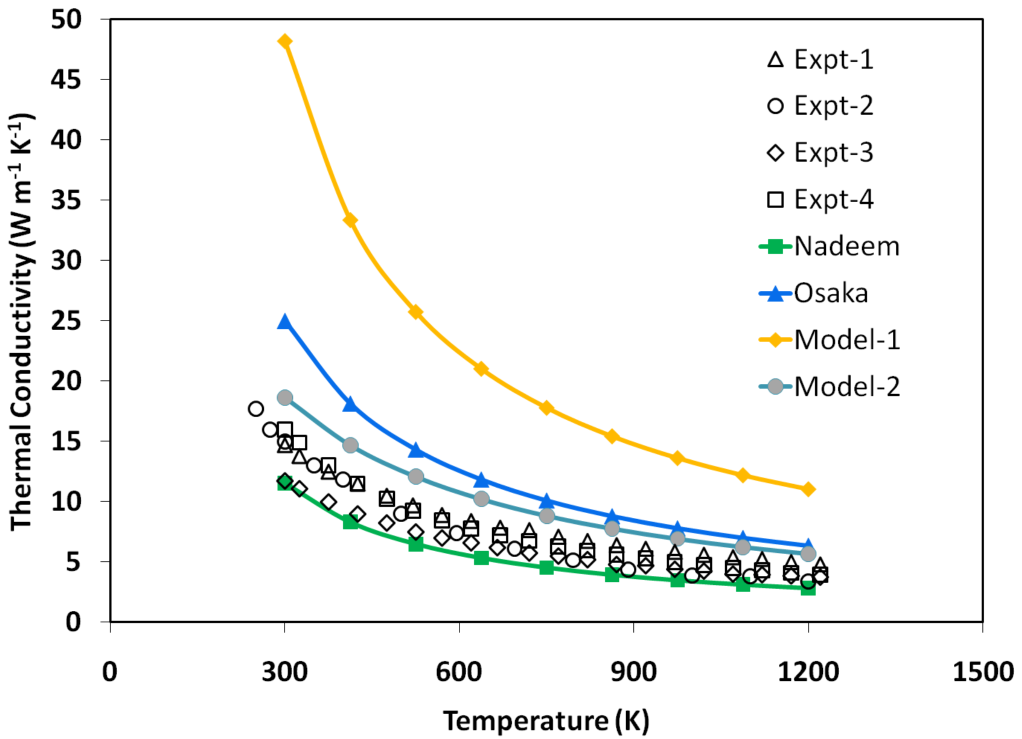
Lattice Parameter [Å]	ThO_2	UO_2
Experiment	5.5997	5.4710
Nadeem	5.5946	5.4749
Osaka	5.5797	5.4441
Model-1	5.5975	5.4547
Model-2	5.5970	5.3889

- The predicted lattice parameters are compared well with the experimental results (Model-2 varies the most)

Hubert *et al.*, Inorg. Chem., 45 (2006) 3887

7. Thermal Properties

- After characterizing static properties of ThO_2, the potentials are used to estimate thermal conductivity



Expt-1
Belle *et al.*, USDOE, DOE/NE-0060, (1984)

Expt-2
Thermal Conductivity – Nonmetallic Solids, Touloukian *et al.* (Eds.), The TRPC Data Series, vol. 2 (1970) Plenum, NY, Washington

Expt-3
Pillai *et al.*, J. Nucl. Mater., 277 (2000) 116

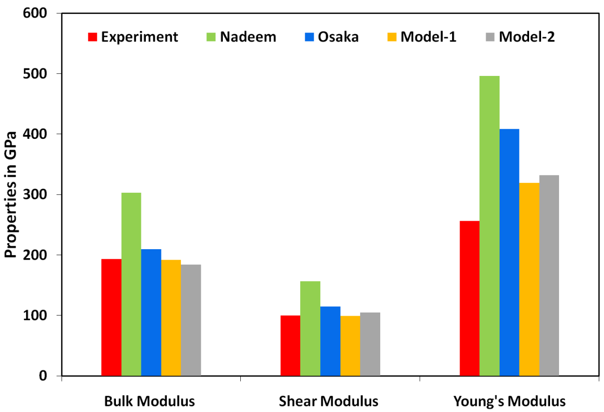
Expt-4
Bakker *et al.*, J. Nucl. Mater., 250 (1997) 1

- The predicted thermal conductivities by Nadeem and Model-2 compare well with the experimental values

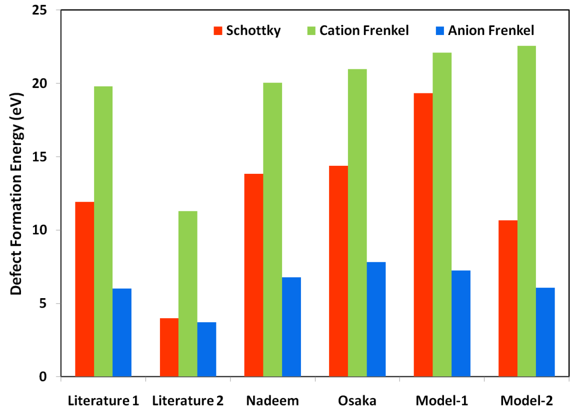
- Osaka and Model-1 overestimates the conductivities

Courtsey: Dr. Alex Chernatynskiy, MSE, University of Florida

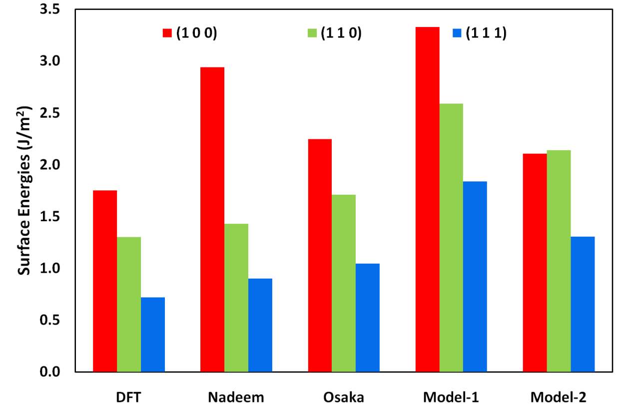
Conclusions



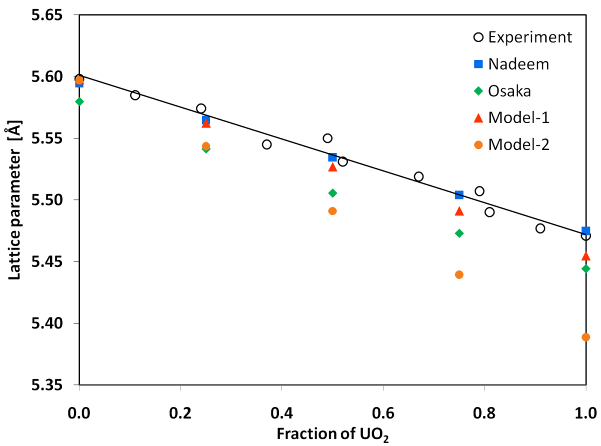
Elastic Properties



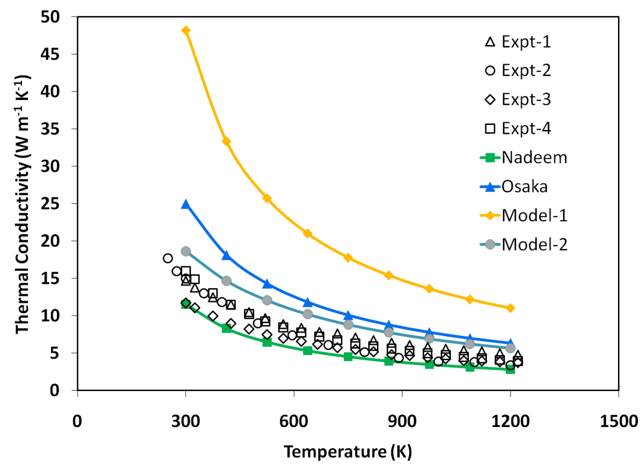
Defect Energetics



Surface Stability



Mixed Oxide



Thermal Conductivity

Outlook

- Once Th-O-U inter-ionic interactions are successfully described, properties of the ThO_2-UO_2 mixed systems will be characterized at the atomic level

- These potentials will be used to investigate
  - Thermal properties (expansion, conductivities)
  - Fission gases and fission product behavior
  - Defect dynamics
  - Radiation damage

- "The database and experience of thorium fuels and thorium fuel cycles are very limited, as compared to UO_2 and $(U,Pu)O_2$ fuels, and need to be augmented before large investments are made for commercial utilization of thorium fuels and fuel cycles." – IAEA Report 2005