Fuels

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Effect of Ce^{4+} and Th^{4+} Ion Substitution in Uranium Dioxide

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ABSTRACT

Uranium dioxide is the most common fuel used in commercial light water nuclear reactors. The fission of the fuel generates fission products (FPs) and minor actinides (MAs), which affects the thermo-physical properties of the fuel. The understanding of the physical and chemical properties of the FPs and MAs is still limited. In this study we have used atomic level simulations to estimate the effect of Ce^{4+} and Th^{4+} ions in urania matrix. Our results show that the structural variation depends on the elastic effect, which is guided by the ionic radius of the substituted ion. Ce^{4+} (ionic radius 0.97 Å) reduces the overall lattice parameter, while Th^{4+} (ionic radius 1.05 Å) increases the overall lattice parameter of the urania matrix (U^{4+} ionic radius 1.00 Å). In addition bulk modulus of the $U_{1-x}Ce_xO_2$ system does not change with substitution while the modulus of $U_{1-x}Th_xO_2$ reduces with an increase in Th^{4+} ion concentration. This observation is in accordance with Vegard's law prediction based on the modulus values of bulk UO_2, CeO_2 and ThO_2 systems.

INTRODUCTION

Uranium dioxide is the most common fuel used in commercial light water nuclear reactors. The fission of uranium based fuels in a light water reactor generates more than 20 fission products (FPs) [1]. In addition, the neutron capture and decay reactions during the fuel cycle produces minor actinides (MAs). These FPs and MAs affect the thermo-physical properties, e.g., thermal conductivity, swelling, creep of the fuel. Lanthanides and actinides are usually dissolved in the host UO_2 matrix. This paper studies the effect of these elements on structure and elastic constants of the host UO_2 matrix using atomistic simulations.

Considering the FPs and MAs, uranium-based fuels can generate Ce, Nd, Pm, Sm, Eu, and Gd in the Lanthanide series and Th, Np, Pu, Am, and Cm in the Actinide series. In this study we have investigated the structural and mechanical properties of UO_2 for 4+ ion (Ce^{4+} or Th^{4+}) substituted urania-systems using atomistic models. Atomic level simulations are successfully used to simulate nuclear materials [2]. In addition it is possible to define the substitution of the species of interest with atomic precision. Since we are interested in investigating the structural and elastic properties of UO_2 and substitution of Ce^{4+} and Th^{4+} in the urania matrix, we have collected relevant interatomic potentials from the literature.

METHODOLOGY

In order to simulate the urania systems with Ce^{4+} and Th^{4+}, we employ the transferable interatomic potentials from the literature which are described in table I. The

overall interactions in urania systems are calculated by a combination of long-range and short-range interactions. The long-range interactions for all the potentials are described by the Coulombic interaction with Ewald sum.

$$V_{Coul}(r_{ij}) = \frac{1}{2}\sum_{i=1}^{N}\left\{\sum_{j\neq i}\frac{q_i q_j}{4\pi\varepsilon_0 r_{ij}}\right\} \quad (1)$$

where N is the total number of ions in the system, ε_0 is the permittivity of free space, q_i, q_j are the magnitude of charges on ions i and j, and r_{ij} is the separation between ions i and j.

Table I. Interatomic potential parameters used to simulate Ce^{4+} and Th^{4+} ions in urania.

Species	Buckingham parameters			Core-shell parameters		
	A [eV]	ρ [Å]	C [eV·Å^6]	q_{core} [e]	q_{shell} [e]	k_2 [eV·Å^{-2}]
Grimes [3]						
$O^{2-} - O^{2-}$	9547.96	0.2192	32.0	0.04	-2.04	6.30
$U^{4+} - O^{2-}$	1761.775	0.35642	0.0	4.10	-0.10	160.00
$Ce^{4+} - O^{2-}$	1809.68	0.3547	20.40	4.20	-0.20	177.84
Nadeem [4]						
$O^{2-} - O^{2-}$	25.41	0.6937	32.32	0.513	-2.513	20.53
$U^{4+} - O^{2-}$	9296.65	0.2796	90.00	5.00	-1.00	134.00
$Th^{4+} - O^{2-}$	8638.50	0.2856	70.00	4.64	-0.64	110.00
$Ce^{4+} - O^{2-}$	7549.87	0.2831	70.00	2.75	1.25	222.00
Arima [5]						
$O^{1.35-} - O^{1.35-}$	919.17	0.332	17.36			
$U^{2.7+} - U^{2.7+}$	2.48 x 10^{+13}	0.072	0.0			
$U^{2.7+} - O^{1.35-}$	55918.39	0.202	0.0			
$Th^{2.7+} - O^{1.35-}$	31321.23	0.220	0.0			
Osaka [6]	Buckingham parameters			Morse parameters		
	A [eV]	ρ [Å]	C [eV·Å^6]	D [eV]	β_{ij} [1/Å]	r*$_{ij}$ [Å]
$O^{1.2-} - O^{1.2-}$	2346.1488	0.32	4.14616			
$U^{2.4+} - U^{2.4+}$	442.2081	0.32	0.0			
$U^{2.4+} - O^{1.2-}$	1018.5705	0.32	0.0	0.78101	1.25	2.369
$Th^{2.4+} - Th^{2.4+}$	17.0261	0.82	0.0			
$Th^{2.4+} - O^{1.2-}$	61.4295	0.57	0.0	1.21500	1.90	2.360

The short-range interactions, which are predominantly repulsive, are given by the Buckingham and/or Morse interactions. The Buckingham potential [7] is given as:

$$V_{Buck}(r_{ij}) = A_{ij}\ \exp\left(-r_{ij}/\rho_{ij}\right) - C_{ij}/r_{ij}^{6} \quad (2)$$

where r_{ij} is the separation between two ions i and j; and A, ρ, and C are free parameters. The Morse potential [8], which is used to describe the covalent bonding in the system, is given as:

$$V_{Morse}(r_{ij}) = D_{ij}\left\{\left[1-\exp\left(-\beta_{ij}\left(r_{ij}-r_{ij}^{*}\right)\right)\right]^2 - 1\right\} \quad (3)$$

where r_{ij} is the separation between two ions i and j; and D, β and r_{ij}^{*} are free parameters.
The Grimes and Nadeem potentials are shell-model potentials whereas Osaka and Arima

potentials are rigid ion models. In the shell model [9], each ion is described by a core and a shell, the sum of whose charges is the ionic charge of each species. A shell model where the core and shell of an atom are coupled by a harmonic spring is given by:

$$V(\omega) = \frac{1}{2} k_2 \omega^2 \quad (4)$$

where ω is the core-shell displacement, and k_2 is the harmonic spring constant. In the rigid ion model the ions are defined by point charges. The Grimes and Nadeem potentials are full charge models (Th^{4+} and O^{2-}), whereas Osaka and Arima are partial charge models.

The General Utility Lattice Program (GULP) [10, 11] was used to predict the structural and elastic properties discussed in this article. All the calculations were performed for a range of Ce^{4+} and Th^{4+} ion substitution with random distribution in the urania matrix (maximum 40% cation substitution). This distribution represents the solid solution condition as reported by Kleykamp [1]. A system size effect on the overall properties is performed and all the results presented in this article are based on a 4 x 4 x 4 supercell system.

RESULTS AND DISCUSSIONS

Before discussing the effect of Ce^{4+} and Th^{4+} ions in urania, it is important to analyze the bulk properties of UO_2 predicted by all the interatomic potentials. Table II lists all the elastic properties of UO_2, which is a re-calculation and summary of the data presented in the literature [2-6] and the references therein. The lattice parameter is predicted within 0.1% of the experimental numbers by most of the potentials, except Arima, which underestimates the lattice parameter by ~0.45%. The individual elastic constants are overestimated for Grimes, Nadeem and Arima; which is typical of interatomic potentials. Osaka is the only potential which underestimated the C_{12} and C_{44}. Hence, the bulk modulus of UO_2 is underestimated by ~12% for Osaka potential.

Table II. Comparison of bulk properties of UO_2 calculated from different interatomic potentials with experiment.

	Experiment [2]	Grimes	Nadeem	Osaka	Arima
Lattice parameter [Å]	5.4698 [12]	5.4681	5.4749	5.4654	5.4449
Lattice Energy (eV/ThO_2)		-104.502	-107.479	-45.589	-51.005
C_{11} [GPa]	389	532 (528)	626 (619)	419 (409)	434 (422)
C_{12} [GPa]	119	122 (119)	187 (179)	59 (56)	120 (111)
C_{44} [GPa]	60	121 (119)	144 (141)	55 (53)	109 (105)
Bulk Modulus [GPa]	204	259 (255)	333 (325)	179 (174)	225 (214)
Shear Modulus [GPa]		150 (148)	171 (168)	90 (88)	126 (123)
Young's Modulus [GPa]	385	486 (484)	540 (538)	405 (397)	382 (376)
Poisson's ration		0.187	0.230	0.124	0.217

Values in the parenthesis are elastic properties predicted at 300 K using individual potentials.

In addition it should be pointed out that the experimental values are measured at a finite temperature while all the simulation results are calculated at 0 K. In order to evaluate

the effect of temperature we have estimated the elastic properties at 300 K (shown within parenthesis in table II). Comparing the 0 K and 300 K results we can conclude that the error associated with the temperature effect is minor.

Effect of 4+ ion substitution

The substitution of 4+ ions in the urania matrix does not change the electrostatic contribution of the overall system. However, the elastic effect due to the ionic radii of the substituted ions will guide the variation of lattice parameter and elastic properties of the urania matrix. The ionic radii of Ce^{4+}, U^{4+} and Th^{4+} are 0.97 Å, 1.00 Å and 1.05 Å respectively [13]. Therefore, Ce^{4+} ions are smaller and Th^{4+} ions are larger than the host U^{4+} ions.

Effect of Ce^{4+} ion substitution

Grimes and Nadeem potentials are used to estimate the effect of Ce^{4+} ion substitution. Following experimental characterization, the change in lattice parameter is evaluated for $U_{1-x}Ce_xO_2$ system where $x \leq 0.4$. The Ce^{4+} ions are randomly distributed in the urania matrix to represent solid solution. Considering the predicted average lattice parameter values at each concentration, a maximum deviation of ±0.0005% is observed for 40% Ce^{4+} substitution. The special quasirandom structure (SQS) is a method to generate structures which mimics the correlation functions of an infinite random system within a finite supercell. The SQS approach is very useful for first-principles calculations, which are limited with system size. The random alloying of Al-Ti system by von Pezold *et al.* [14] shows that the SQS method for a 2 x 2 x 2 (32 atom) supercell results in similar elastic properties as a randomly distributed alloy system with 4 x 4 x 4 supercell (256 atoms). In this study we have considered the random distribution of Ce^{4+} and Th^{4+} ions in a 4 x 4 x 4 supercell containing 768 atoms.

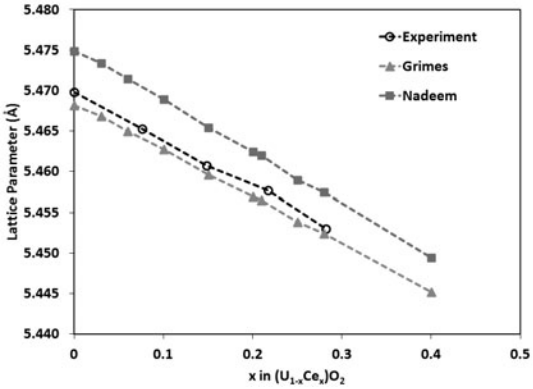

Figure 1. (Color online) Variation of lattice parameter due to 4+ ion substitution in $U_{1-x}Ce_xO_2$ system

Figure 1 illustrates the comparison of the absolute change in lattice parameter predicted by the two potentials with experiment. The lattice parameter predicted by Grimes [3] and Nadeem [4] for pure UO_2 (x = 0 in figure 1) are 5.4681 Å and 5.4749 Å respectively. The prediction from Grimes agrees more closely with the experimental UO_2 lattice parameter of 5.4698 Å (table II). With Ce^{4+} ion substitution, the two potentials give the same change in parameter, with the offset being equal to the initial difference in the lattice parameter for pure UO_2. Thus, using the atomistic models we have successfully calculated the variation in lattice parameter of Ce^{4+} ion substituted urania system. The results show that the elastic effect due to the substitution of a smaller ionic radius cation (Ce^{4+} = 0.97 Å compared to U^{4+} = 1.00 Å) reduces the overall lattice parameter of the system.

The $U_{1-x}Ce_xO_2$ system is very interesting as the fission of urania fuel generates cerium, which is highly soluble in the urania matrix. Also Ce and Pu ions show similar ionic radii and oxidation states. Therefore, ceria has been investigated as a surrogate for urania-plutonia mixed oxide fuels [15]. The incorporation of ceria in the urania matrix can affect various thermo-physical properties such as elastic properties, thermal conductivity, ionic diffusion, phase stability. In order to characterize the effect of Ce^{4+} ion substitution on the overall properties of the urania matrix, we have estimated a physical parameter which is purely based on the change in the stoichiometry of the fuel.

Since lattice parameter of the urania matrix changes due to substitution at a constant temperature and oxygen stoichiometry, it is possible to estimate the lattice variation with a physical parameter known as chemical expansion. Similar to thermal expansion, chemical expansion measures the change in lattice parameter due to the change in chemical formula of the urania matrix. While temperature is the guiding variable for thermal expansion, the substituted ionic species is the guiding factor for chemical expansion. For most of the materials the thermal expansion is positive, while chemical expansion can be either positive or negative depending on the ionic radii and charge state of the substituted ions. Therefore, the chemical expansion for the $U_{1-x}Ce_xO_2$ system can be defined as [16]

$$\varepsilon_C = \left.\frac{(a - a_0)}{a_0}\right|_{T=\text{Constant}} \tag{5}$$

where a is the lattice parameter measured at any concentration, and a_0 is the lattice parameter of UO_2 perfect lattice. Table III lists the chemical expansion with Ce^{4+} ion concentration for the empirical models. For a single crystal, a variation in lattice parameter is the same as the variation in length. Thus, for all the compositions analyzed $(a - a_0) / a_0 = (L - L_0) / L_0$, where L is the length of the supercell measured with substituted ions, and L_0 is the length of the supercell for perfect UO_2.

Effectively, the reduction in lattice parameter of the urania matrix may be achieved by a change in temperature. The change in temperature (ΔT_{eq}) necessary to achieve the same amount of variation in pure UO_2 as observed for the substitution of different concentration of Ce^{4+} ions may be calculated as:

$$\varepsilon_C = \alpha_{T,bulkUO_2}\,\Delta T_{eq} \tag{6}$$

where, ε_c is the chemical expansion calculated from the simulations, and $\alpha_{T,bulkUO2}$ is the coefficient of thermal expansion reported for bulk UO_2 11.8 x 10^{-6} K^{-1} [17] from experiment.

The ΔT_{eq} values estimated for different concentration of Ce^{4+} ions is reported in table III. For example, the ε_c observed for $U_{0.79}Ce_{0.21}O_2$ system is equivalent to reducing the temperature by ~181 - 200 K for bulk UO_2.

Table III. Chemical expansions calculated for Ce^{4+} ion substitution in $U_{1-x}Ce_xO_2$ system using Grimes and Nadeem potentials.

	x	a_0 (Å)	a (Å)	Δa (Å)	ε_C	ΔT_{eq} (K)
Grimes	0	5.4681				
	0.06		5.4650	-0.0031	-0.0006	-49
	0.15		5.4596	-0.0085	-0.0016	-132
	0.21		5.4565	-0.0117	-0.0021	-181
	0.28		5.4524	-0.0157	-0.0029	-244
Nadeem	0	5.4749				
	0.06		5.4714	-0.0035	-0.0006	-54
	0.15		5.4655	-0.0094	-0.0017	-146
	0.21		5.4620	-0.0129	-0.0024	-200
	0.28		5.4575	-0.0174	-0.0032	-270

Effect of Th^{4+} ion substitution

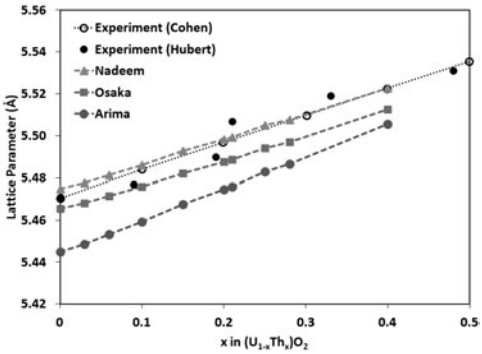

Figure 2. (Color online) Variation of lattice parameter due to 4+ ion substitution in $U_{1-x}Th_xO_2$ system. The experimental data are obtained from Cohen *et al.* [18] and Hubert *et al.* [19]. The variation in experimental lattice parameter is linear with Th-stoichiometry.

Similar analysis is performed for Th^{4+} ion substitution in the UO_2 matrix with the variation in lattice parameter presented in figure 2. We followed the structural arrangement of $U_{1-x}Ce_xO_2$ system to build the input structures for $U_{1-x}Th_xO_2$ system. Comparing the results with experiment [18, 19], Nadeem potential does a very good job in predicting the quantitative variation of lattice parameter with Th^{4+} ion substitution. Osaka potential predicts a relatively smaller slope for the $U_{1-x}Th_xO_2$ system compared to experiment. Arima potential shows the largest deviation in bulk UO_2 lattice parameter. However, the slope of the lattice parameter – Th^{4+} concentration relationship is well compared with experiment. Here the

lattice parameter of urania matrix increases with Th^{4+} ion substitution, contrary to Ce^{4+} ion substitution. This response is also due to the elastic effect. Th^{4+} ions are about 5% larger than the U^{4+} ions. Substitution of Th^{4+} ions creates local tension in the lattice, thereby increasing the overall lattice parameter. The ε_c, and ΔT_{eq} values for different potentials and compositions are calculated in the same manner as discussed for Ce^{4+} systems (using Eqs. 5 and 6).

Summary of Ce^{4+} and Th^{4+} ion substitution on lattice parameter

In order to directly compare ceria and thoria substitution, we took one nominal concentration (20%) of the dissolved ions in UO_2. Figure 3 shows the percentage change in lattice parameter predicted for $U_{1-x}A_xO_2$, where x=0.2, and A = Ce and Th. For 20% substitution, the lattice parameter decreases by ~0.22 ± 0.01 % for ceria and increases by ~0.46 ± 0.08 % for thoria. The results clearly indicate that the variation in lattice parameter for 4+ ion substitution is guided by the ionic radius (elastic effect) of the substituted ion.

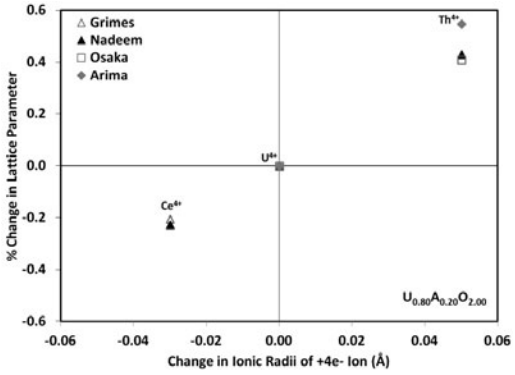

Figure 3. (Color online) Variation of lattice parameter due to Ce^{4+} and Th^{4+} ion substitution in $U_{1-x}A_xO_2$ system, where x = 0.20.

Effect of Ce^{4+} and Th^{4+} ion substitution on bulk modulus

The experimental bulk modulus of CeO_2 and ThO_2 are listed in table IV. We have used the experimental elastic constants (C_{11} and C_{12}) [20-22] to estimate the bulk modulus of UO_2, CeO_2 and ThO_2, where the bulk modulus is given as $(C_{11} + 2C_{12}) / 3$. This approach allows us to directly compare the single crystal bulk modulus values predicted from the simulations with experimental bulk modulus. The analysis of experimental bulk modulus values show that there is almost no variation in bulk modulus between pure UO_2 and CeO_2 and the bulk modulus reduces for bulk ThO_2 compared to UO_2. The predicted bulk modulus values of pure UO_2, CeO_2, and ThO_2 with empirical potentials follow the experimental trend (table IV). However, Osaka potential predicted a higher bulk modulus for ThO_2 compared to UO_2, which is not surprising since it severely underestimated (~50%) C_{12} elastic constant of bulk UO_2 (table II). Using Vegard's law for the substituted systems, we should expect almost

no variation for $U_{1-x}Ce_xO_2$ system and a reduction in bulk modulus for $U_{1-x}Th_xO_2$ system.

Table IV. Bulk modulus values calculated for UO_2, CeO_2 and ThO_2 by all the interatomic potentials. The results are compared to experimental results.

in GPa	UO_2	CeO_2	ThO_2
Experiment*	209-212 [21]	204 [20]	193 [22]
Grimes	259	268	
Nadeem	333	333	303
Osaka	179		206
Arima	225		192

*Calculated using elastic constants reported in the experiment. The bulk modulus values measured directly in the experiment are 207±2 GPa for UO_2 [23], 230±10 GPa for CeO_2 [24], and 198±2 GPa for ThO_2 [23].

Since Nadeem is the only potential which described both Ce^{4+} and Th^{4+} ions, the variation in bulk modulus with concentration is discussed for this potential. Figure 4 shows the effect of substitution on the bulk modulus for $U_{1-x}Ce_xO_2$ and $U_{1-x}Th_xO_2$ system using Nadeem potential. The results clearly show almost no effect on the bulk modulus for $U_{1-x}Ce_xO_2$ and a gradual reduction for $U_{1-x}Th_xO_2$ system. This is in agreement with the Vegard's law prediction from the experimental bulk modulus reported in table IV.

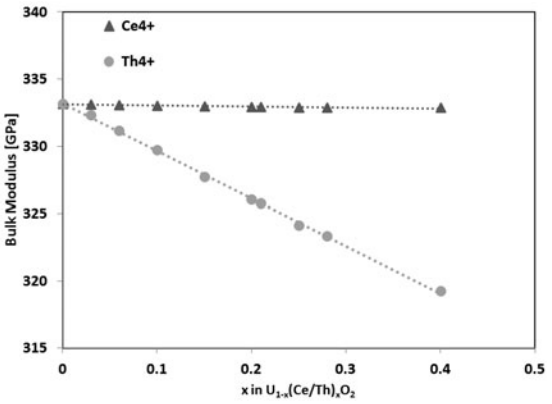

Figure 4. (Color online) Variation of bulk modulus for a range of Ce^{4+} and Th^{4+} ion substitution in urania matrix using Nadeem potential. Substitution of Ce^{4+} shows very minimal variation in bulk modulus, while the modulus decreases with Th^{4+} ion substitution in urania.

CONCLUSIONS

This study presented the effect of substitution on the structural and elastic properties of $U_{1-x}A_xO_2$ system (A = Ce and Th). Using atomistic simulations with empirical potentials