Energetics and Defect Clustering Trends for Trivalent Rare Earth Cations Substituted in UO_2

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Abstract

Trends in the energetics and defect clustering tendencies for UO_2 compounds substituted with trivalent rare earth cations (M^{3+}) are investigated computationally using methods based on density functional theory. Higher energetic stability of $\text{U}_{1-x}\text{M}_x\text{O}_{2-0.5x}$ solid solutions relative to constituent oxides and increased preference for higher oxygen coordination around the trivalent cation are found with increasing size of the M^{3+} species. The implications of the computational results for the effect of trivalent fission products on oxygen ion mobility in spent fuel are discussed.

1. Introduction

A key concern of the nuclear materials community is the assurance of safe long-term storage of spent nuclear fuel. In this context, an issue that has received considerable attention is the effect that the substitution of U^{4+} cations by more soluble trivalent rare earth fission product cations (M^{3+}) has on the rate of oxidation and oxidative corrosion in uranium oxide (UO_2) [1, 2, 3, 4, 5, 6, 7]. In particular, recent studies [8, 1] attributed the trend towards decreased oxidative dissolution rates with increasing burnup, to the interactions between cations and charge-compensating defects (i.e., oxygen vacancies) in the formation of stable defect clusters. The authors in ref.

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[1] found evidence of such defect clusters with increasing trivalent rare earth doping level using Raman spectroscopic techniques. These clusters may form by the thermodynamically-favorable association of trivalent substitutional atoms (M^{3+}) with charge-compensating oxygen vacancies. The formation of such stable clusters has been hypothesized to reduce the concentration of mobile (unbound) oxygen vacancies, and thus is expected to lead to a lowering of oxygen ion diffusivity [1, 2, 8]. Cluster formation may thus be expected to reduce the rate of oxidation and eventual dissolution of the fuel in repository waste storage containers for both thermodynamic (by stabilizing the solid solution) and kinetic (by reducing oxygen mobility) reasons.

While the effect of rare earth substitution on oxygen chemical potentials, lattice constants and thermal conductivity in UO_2 has been well studied (e.g., [9, 10] and references therein), and initial experimental and computational studies of formation energetics in urania-rare earth solid solutions have been recently reported [11, 12], explicit investigations of defect-clustering behavior has been addressed in relatively few studies [12, 13, 14]. Computational modeling based on classical ionic pair potentials [14] and defect chemistry models [13] concludes that defect clustering is energetically favorable (as it must be in order for clustering to occur, because clustering decreases the entropy); however, a detailed study of systematic trends in energetics and clustering tendencies with varying concentrations and types of rare earth trivalent cations (M^{3+}) has not been reported to the best of our knowledge. As a consequence, understanding the effects of defect clustering on solid-solution stability and oxygen vacancy mobilities, which is key in understanding fuel oxidation/corrosion behavior, remains incomplete.

Previous studies [15, 16, 17] on trivalent-doped fluorite systems concluded that oxygen vacancy mobility is highest when there is little energetic preference for a particular defect ordering arrangement. In a previous computational study by the authors [12] employing density-functional-theory-based methods, different energetic properties and defect clustering tendencies were obtained for oxygen-vacancy-charge-compensated UO_2 systems ($U_{1-x}M_xO_{2-0.5x}$) containing the smallest and largest rare earth trivalent cations (M), Y and La, respectively. That work suggested that the magnitude and nature of vacancy interactions with trivalent cations are influenced by the ionic radius of the M^{3+} species. However, the results were based on calculations for only two rare earth cations, and further work is warranted to better establish and understand such trends. In the present work, the energetics are further investigated by considering a series of trivalent rare earth cations

substituted in UO_2 solid solutions with charge compensating oxygen vacancies. Specifically, we consider systems of composition $\text{U}_{0.5}\text{M}_{0.5}\text{O}_{1.75}$, with M being Dy^{3+} (1.03 Å, Shannon radius with eightfold coordination [18]), Gd^{3+} (1.05 Å), Eu^{3+} (1.07 Å), Sm^{3+} (1.08 Å), Pm^{3+} (1.09 Å), Nd^{3+} (1.11 Å), Pr^{3+} (1.13 Å), Ce^{3+} (1.14 Å) and La^{3+} (1.16 Å). The results reveal clear trends that are discussed in the context of models that have been proposed for other trivalent-doped fluorite-structured oxide systems. We note that in the current calculations we do not consider uranium in oxidation states higher than +4, so the total vacancy concentration is fixed by the amount of rare earth substitution, with no oxygen interstitials present.

2. Computational Methodology

The computational approach employed in this work has been described previously [12], and is summarized briefly in this section. The lowest-energy structure for a given concentration of a particular M^{3+} species (and corresponding number of oxygen vacancies) is determined by calculation of many hypothetical structures with different configurations of U^{4+} and M^{3+} on the cation sublattice, and oxygen ions and vacancies on the anion sublattice of the fluorite structure. This involves the use of ionic pair potential models [19, 20, 15, 21, 22] to screen out configurations with large energies, and the use of DFT-based methods to determine energies of the lowest-energy structures. The DFT energies were obtained within the formalism of the projector augmented-wave (PAW) method [23, 24] and the Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation (GGA) [25, 26] as implemented in the Vienna *ab initio* simulation package (VASP) [27, 28]. A Hubbard-U correction in the DFT+U formalism of Dudarev *et al.* [29] with $U_{\text{eff}} = U - J = 4.00$ eV was employed for the treatment of the uranium $5f$ orbitals in this study. We employ the approach by Meredig *et al.* [30] involving a gradual ramping up of the Hubbard-U parameter. In our previous work [12] we compared this ramping method to the Occupation Matrix Control (OMC) method by Dorado *et al.* [31], in which we sampled 61 different occupation matrices for a trivalent doped fluorite UO_2 system charged-compensated with oxygen vacancies, and found that the ramping method gave rise to a configuration with a lower total energy than that derived using OMC. The PAW potentials used in this work are U, O, Dy_3, Gd_3, Eu_3, Sm_3, Pm_3, Nd_3, Pr_3, and Ce_3 in the VASP PBE library, where the “_3” denotes that the occupied $4f$ orbitals in the trivalent oxidation state of the rare-earth ions are

treated as core electrons. We employ a plane-wave cutoff energy of 500 eV, and the Brillouin zone is sampled using the Monkhorst-Pack scheme with 4 x 4 x 4 k-point meshes. Atomic positions were relaxed with no symmetry constraints until residual forces were below approximately 20 meV/Å. From convergence checks with respect to plane-wave cutoff and k-point sampling we estimate the formation enthalpies are converged at the level of a few tenths of a kJ/mol-cation.

The formation enthalpy for the $U_{0.5}M_{0.5}O_{1.75}$ compounds considered here, with respect to its constituent oxides, is defined as

$$\Delta H_f = E(U_{0.5}M_{0.5}O_{1.75}) - [E(UO_2) - E(MO_{1.5})]/2, \quad (1)$$

where the energies (E) are expressed per cation. In Eq. 1, $E(UO_2)$ is for fluorite-structured UO_2 (calculated here using a 12-atom unit cell with 1k antiferromagnetic order), and $E(MO_{1.5})$ is for M_2O_3 in the experimentally observed (i.e., room temperature) cubic bixbyite (C-type sesquioxide) or hexagonal (A-type) structure. The experimentally observed C-type sesquioxides are Y_2O_3 , Dy_2O_3 , Gd_2O_3 , Eu_2O_3 , Sm_2O_3 , and Pm_2O_3 , and the A-type sesquioxides are Nd_2O_3 , Pr_2O_3 , Ce_2O_3 , and La_2O_3 [32].

In this study we investigated M^{3+} substitution levels that are high relative to typical fission product yields. This was done for several reasons. It allows for the practical application of high throughput calculations for systems with various dopant species. It also allows for direct comparison with previous results that considered $M^{3+} = Y^{3+}$ and La^{3+} , which were compared to other fluorite oxide systems where high M^{3+} substitution levels are common [12].

3. Results and Discussion

We begin by analyzing the calculated formation enthalpies for the lowest-energy structures of $U_{0.5}M_{0.5}O_{1.75}$ plotted as a function of the Shannon ionic radius of the M^{3+} cation for eightfold coordination (Fig. 1). Positive values of ΔH_f indicate that phase separation into UO_2 and M_2O_3 is favored (endothermic) at low temperatures, whereas negative values of ΔH_f indicate a compound forming tendency (exothermic). Figure 1 illustrates that compound formation is preferred (weakly) only for the largest M^{3+} cation sizes, while the formation enthalpy is increasingly positive as the M^{3+} ionic radius decreases.

The magnitudes of the formation enthalpies are relatively small in comparison to the magnitude of the configurational entropy contribution to the

Figure 1: Formation enthalpies of $\text{U}_{0.5}\text{M}_{0.5}\text{O}_{1.75}$ structures are shown for the lowest-energy fully relaxed structures of all compositions enumerated in this study. Calculations for $\text{M}=\text{Y}$ and La were taken from ref. [12] for comparison.

Gibbs free energy at temperatures relevant to the processing and service of nuclear fuels. For example, for a $\text{U}_{1-x}\text{M}_x\text{O}_{2-0.5x}$ system with $x = 0.5$ the ideal configurational entropy leads to a contribution of -12 kJ/mol-cation to the Gibbs free energy of formation at $T=1000$ K, which is larger than the magnitude of ΔH_f for all the trivalent species plotted in Fig. 1. Consequently the formation free energy is expected to be negative at such temperatures for all of the systems considered in this work. This result is consistent with the fact that rare-earth fission products typically show solubility in UO_2 over wide composition and temperature ranges [33].

We consider now the defect-clustering tendencies in $\text{UO}_2\text{-M}_2\text{O}_{1.5}$ systems by examining the nature of preferred interactions between M^{3+} and oxygen vacancies. The formation enthalpies of three low energy structures with one, two, and three M^{3+} -oxygen vacancy nearest neighbors averaged over all M^{3+} ions in the system (two total) are compared for each M^{3+} species in Fig. 2, denoted by the blue, green, and red circles, respectively. The structural motifs of the three structures are represented in Fig. 3.

Figure 2: The formation enthalpies for selected structures containing, one, two, and three trivalent cation nearest neighbors to an oxygen vacancy are shown. Calculations for $M=Y$ and La were taken from ref. [12] for comparison.

The results in Fig. 2 demonstrate that the small and large M cations display qualitatively different preferences; the formation enthalpies of systems containing smaller and larger M cations decrease (more exothermic) and increase (more endothermic), respectively, with increasing number of M^{3+} -vacancy neighbors. For an M cation size of $1.09 \text{ \AA}$ ($M=Pm$), the formation enthalpies for the three configurations are nearly degenerate, i.e. there is little energetic preference for M^{3+} -oxygen vacancy and U^{4+} -oxygen vacancy nearest neighbors. Similar observations of a trivalent cation size for which there is an apparent lack of preferred clustering tendencies has been found in previous calculations for CeO_2 [15, 34] and ZrO_2 [16, 35] fluorite structures.

The trends in Figs. 1 and 2 are consistent with models presented in the literature to explain similar results in other fluorite-structured oxide systems [36, 37]. We first consider the trend of lower formation enthalpy (more exothermic) with increasing size of the M^{3+} rare earth ion in Fig. 1. U^{4+} prefers an eightfold oxygen ion coordination environment. While of similar

Figure 3: Structural motifs of low energy structures containing one (left), two (middle), and three (right) M^{3+} -oxygen vacancy nearest neighbors.

size to U^{4+} , the rare-earth M^{3+} cations considered in this work generally prefer a lower coordination environment due to their lower valence. Upon formation of the defected fluorite compound $U_{1-x}M_xO_{2-0.5x}$, U^{4+} in general must lower its coordination environment relative to its coordination in pure UO_2 due to the formation of charge compensating oxygen vacancies; concomitantly, M^{3+} must increase its coordination environment relative to pure M_2O_3 . Increasing energetic stability of the $U_{1-x}M_xO_{2-0.5x}$ compounds with increasing size of the M^{3+} cation can then be understood as resulting from the lower energetic penalty associated with increasing the oxygen coordination around larger rare earth ions.

The trend in Fig. 2 shows that the preference for oxygen vacancy nearest neighbors decreases with increasing size of the M^{3+} cations, which is due to larger ions preferring higher oxygen ion coordination. The preference for a particular defect ordering arrangement, i.e. for rare earth cations with size smaller or larger than the radius at the crossover point, is suggestive of defect clustering in short range ordered solid solutions. This clustering effect is expected to lower oxygen ion mobility, as discussed previously in the context of ionic conductivity in fluorite-structured solid electrolytes [38], by limiting the number of oxygen vacancies available for oxygen to diffuse into the solid. This kinetic limitation of oxygen incorporation due to clustering is believed to reduce oxidation and subsequent dissolution of spent fuel [8, 1]. The work in ref. [1] which found evidence of stable defect clusters and reduced fuel dissolution with increasing $M=Gd$ and Dy dopants is consistent with our calculations which show strong preference for ordering/clustering for these systems (Fig. 2), supporting the hypothesis that clustering is present and that it kinetically limits fuel corrosion.

4. Summary

A systematic DFT study of UO_2 compounds substituted with trivalent rare earth cations (M^{3+}) found higher energetic stability of $\text{U}_{1-x}\text{M}_x\text{O}_{2-0.5x}$ solid solutions relative to constituent oxides with increasing size of the M^{3+} species. Furthermore, an investigation of the defect ordering tendencies shows an increasing preference for higher oxygen coordination around the rare earth ions with increasing size of these M^{3+} species. Compounds with ionic radius of the M^{3+} species smaller or larger than 1.09 Å are found to have energetically preferred defect ordering arrangements. Systems with preferred defect ordering arrangements are suggestive of defect clustering in short range ordered solid solutions, which is expected to limit oxygen ion mobility and therefore the rate of oxidation of spent nuclear fuel.

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