A Combined Calorimetric and Computational Study of the Energetics of Rare Earth Substituted
UO₂ Systems

Lei Zhang^{a,b}, Jonathan M. Solomon^c, Mark Asta^{b,c}, and Alexandra Navrotsky^{a,b}

^aPeter A. Rock Thermochemistry Laboratory and NEAT ORU, University of California Davis

Davis CA 95616

^bDepartment of Chemical Engineering and Materials Science, University of California Davis

Davis CA 95616

^cDepartment of Materials Science and Engineering, University of California Berkeley

Berkeley CA 94720

Abstract

The energetics of rare earth substituted UO_2 solid solutions ($\text{U}_{1-x}\text{Ln}_x\text{O}_{2-0.5x+y}$, where Ln = La, Y, and Nd) are investigated employing a combination of calorimetric measurements and density functional theory based computations. Calculated and measured formation enthalpies agree within 10 kJ/mol for stoichiometric oxygen/metal compositions. To better understand the factors governing the stability and defect binding in rare earth substituted urania solid solutions, systematic trends in the energetics are investigated based on the present results and previous computational and experimental thermochemical studies of rare earth substituted fluorite oxides ($\text{A}_{1-x}\text{Ln}_x\text{O}_{2-0.5x}$, where A = Hf, Zr, Ce, and Th). A consistent trend towards increased energetic stability with larger size mismatch between the smaller host tetravalent cation and the larger rare earth trivalent cation is found for both actinide and non-actinide fluorite oxide systems where aliovalent substitution of Ln cations is compensated by oxygen vacancies. However, the large exothermic oxidation enthalpy in the UO_2 based systems favors oxygen rich compositions where charge compensation occurs through the formation of uranium cations with higher oxidation states.

Keywords: Formation enthalpy; fluorite oxide; calorimetry; DFT

1. Introduction

The structural and thermochemical properties of rare earth substituted UO_2 solid solutions have been studied extensively due to their relevance in optimizing nuclear fuel performance [1]. Trivalent rare earth cations are common fission products that are soluble with UO_2 over wide compositions ranges [2]. Both experimental [3-5] and thermodynamic modeling studies [2,6,[7] have been applied to better understand and predict thermochemical and thermophysical properties of these systems. In particular, oxygen partial molar free energies [3], phase relations [4,5,8-10], composition dependent lattice parameters [11-13], and electronic properties [16] have been previously reported for a variety of different rare-earth substitutions.

Despite extensive previous work, direct experimental measurements of the energetics of rare earth substituted urania solid solutions have become available only relatively recently [18]. In a recent paper [18] two of the authors report the formation enthalpies of La, Y, and Nd doped uranium oxides over a wide range of dopant concentrations and oxygen stoichiometries (mostly hyperstoichiometric), measured by high temperature oxide melt solution calorimetry. The oxidation enthalpies of $\text{Ln}_x\text{U}_{1-x}\text{O}_{2-0.5x+y}$ were found to be similar to that of pure UO_2 to UO_3 . The strongly exothermic formation enthalpies of these oxygen - rich rare earth doped uranium oxides explains the difficulties in preparing samples in the oxygen deficient region. The enthalpies of formation from constituent oxides (Ln_2O_3 , UO_2 , and UO_3) become increasingly exothermic with increasing rare earth substitution. The enthalpies show only small variations with oxygen content in the oxygen excess (hyperstoichiometric) region.

Computational investigations of the energetics of rare earth substituted urania solid solutions have also been reported only relative recently [20]. In contrast to the experimental investigations, which focused on stoichiometric and hyperstoichiometric oxygen to metal ratios,

the computational work published to date investigated hypostoichiometric compositions where charge compensation occurs through oxygen vacancies. The focus on such compositions in the computational work was motivated by the desire to understand trends in the binding of rare earth cations and vacancies, which have been reported as a central issue in understanding the influence of burnup on the rate of oxidative corrosion in spent nuclear fuel [22]. In the present work the computational studies are extended to consider compositions with oxygen stoichiometries varying from the limit of oxygen vacancy compensation up to stoichiometric oxygen/metal ratios. We note that, due to the importance of oxygen clustering at hyperstoichiometric compositions [26], the phase space underlying the energetics of rare earth substituted urania solid solutions in this composition range is challenging to model by first principles calculations, and beyond the scope of the present work. Nevertheless, the extension of the computational studies to stoichiometric oxygen/metal ratios enables direct comparisons between calculated and measured data near these compositions. By combining the calculated results with the experimental data, which are limited to near stoichiometric to hyperstoichiometric compositions, a more complete picture of the effect of oxygen content on the energetic stability of rare earth - urania solid solutions can be obtained.

Thus the goal of this paper is to combine, for the first time, computational and experimental methods to study the energetics of rare earth substituted urania solid solutions, using theory for compositions where experiment is difficult, and vice versa, while making comparisons for compositions where theory and experiment overlap by extending calculations to more oxygen - rich compositions. We also explore systematic energetic trends in vacancy compensated systems, based on present and previous computational [28] and experimental [35] studies, in order to improve overall understanding of the factors governing the stability of these

systems. The key findings are as follows. (1) Favorable agreement between computation and experiment is found at compositions where direct comparisons can be made. (2) Trends for compositions that are fully oxygen vacancy compensated in urania – based systems are consistent with those in other fluorite systems and show a strong dependence on the mismatch between host and rare earth cation size. (3) UO_2 is distinguished from other fluorite systems by the very large and exothermic oxidation enthalpy due to the energetic stability of the higher oxidation states of uranium.

2. Methods

2.1 Experimental procedures

The rare earth doped uranium oxide solutions ($\text{Ln}_x\text{U}_{1-x}\text{O}_{2-0.5x+y}$, where $\text{Ln} = \text{La}, \text{Y},$ and Nd) were prepared by a coprecipitation method followed by sintering at 1100 – 1450 °C under reducing atmosphere. The sintered materials were characterized carefully to obtain a single-phase homogeneous fluorite oxide. Their phases were examined by XRD to confirm the presence of only a single fluorite phase, chemical compositions were determined by electron microprobe analysis to confirm homogeneous phases, and uranium oxidation states measured by Ce(IV)-Fe(II) back-titration after dissolution of the samples in warm acid mixtures added with excess Ce(IV) solutions. The drop solution enthalpies were measured by dropping samples into a molten oxide solvent ($3\text{NaO}\cdot 4\text{MoO}_3$) in a high temperature calorimeter at 700 °C and the enthalpies of formation at room temperature from oxides were calculated. A detailed description of the preparation, characterization, and calorimetry of these materials can be found in ref. [18]. The calorimetric study showed that the formation enthalpies of the rare earth doped uranium oxides from rare earth oxide and a mixture of UO_2 and UO_3 that gives the observed oxygen content are

approximately independent of the oxygen content in the oxygen excess region. This allows simple and accurate estimation of the enthalpy of formation of a sample with any given rare earth content and oxidation state in the oxygen excess region.

2.2 Computational methods

The computational approach has been described previously in work focused on the study of vacancy-compensated urania – rare earth oxide solid solutions [19]. This approach is summarized briefly in this section, with an emphasis on describing the extensions of the methods to consider higher oxygen concentrations where charge compensation involves the formation of higher oxidation states of uranium. An analysis of the electronic structure and local magnetic moments suggests that in the calculations the higher oxidation states of uranium are U^{5+} .

The lowest energy structure for a given concentration of a particular Ln^{3+} species (and corresponding number of oxygen vacancies) is determined by calculation of many hypothetical arrangements of the uranium and rare earth species on the cation sublattice and oxygen and vacancies on the anion sublattice. The cation sublattice contains host and rare earth species U^{4+} , U^{5+} and Ln^{3+} , and the anion sublattice contains host and vacancy species, O^{2-} and O_{vac} . At hypostoichiometric compositions the substitution of two U^{4+} by two Ln^{3+} can be charge compensated by one O_{vac} . For a stoichiometric oxygen/metal ratio equal to 2, charge compensation can occur by oxidation of U^{4+} to U^{5+} for every one Ln^{3+}/U^{4+} substitution, as illustrated in Fig. 1. Systems with compositions that are intermediate between fully oxygen vacancy charge - compensated and fully U^{5+} charge - compensated contain both oxygen vacancies and U^{5+} ions.

We employ a structure enumeration technique developed for cluster expansion based studies of alloy thermodynamics, considering supercells consisting of up to eight formula units,

employing an algorithm by Hart and Forcade [36] that is implemented in the alloy theoretic automatic toolkit (ATAT) [38]. We consider three different oxygen to metal ratios, namely “reduced” (fully charge-compensated with oxygen vacancies), “stoichiometric” (fully charge-compensated with U^{5+} ions), and “intermediate” (charge-compensated by both oxygen vacancies and U^{5+} ions). Specifically, the “reduced regime” considers $U_4Ln_2O_{11}$ (six formula units: 4 U^{4+} ions, 2 Ln ions, 11 O ions, and 1 O_{vac}) and $U_2Ln_2O_7$ (four formula units: 2 U^{4+} ions, 2 Ln ions, 7 O ions, and 1 O_{vac}), yielding 117 and 27 symmetry - distinct structures, respectively. The “stoichiometric” regime considers $U_4Ln_2O_{12}$ (six formula units: 2 U^{4+} ions, 2 U^{5+} ions, 2 Ln ions, and 12 O ions) and $U_2Ln_2O_8$ (four formula units: 2 U^{5+} ions, 2 Ln ions, and 8 O ions), yielding 100 and 5 symmetry-distinct structures, respectively. The “intermediate regime” considers $U_4Ln_4O_{15}$ (eight formula units: 2 U^{4+} ions, 2 U^{5+} ions 4 Ln ions, 15 O ions, and 1 O_{vac}), yielding 7296 symmetry-distinct structures. The compositions considered for the calculations in this work are summarized in Table 1.

After enumerating the different possible configurations at the different oxygen concentrations we use ionic pair potential models [44] to screen out configurations with large energies, and employ density functional theory (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 [46] and the Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation (GGA) [48] as implemented in the Vienna ab initio Simulation Package (VASP) [50]. A Hubbard-U correction in the DFT+U formalism of Dudarev et al. [51] with $U_{eff} = U - J = 4.00$ eV was employed for the treatment of the uranium 5f orbitals in this study. We employ the approach by Meredig et al. [52] involving a gradual ramping up of the Hubbard-U parameter. In our previous work [19] we compared this ramping method to the

Occupation Matrix Control (OMC) method by Dorado et al. [53] and found that the ramping method gave rise to a configuration with a lower total energy than that derived using OMC for the 61 matrices that were sampled.

The PAW potentials used in this work are U, O, Y_{sv}, La and Nd₃ 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.

3. Results

For rare earth doped uranium oxide solid solutions formed from constituent oxides, the formation reaction can be written as:

The corresponding formation enthalpy to be calculated is thus defined as

$$\Delta H_f = H[U_{1-x}Ln_xO_{2-0.5x+y}] - (1 - x - y)H[UO_2] - xH[LnO_{1.5}] - yH[UO_3] \quad (2)$$

where x is the Ln^{3+} substitution fraction, $H[A]$ is the enthalpy per formula unit of compound A, and y is the oxygen content, which is related to the oxygen to metal ratio (O/M) by

$$y = O/M + 0.5x - 2 \quad (3)$$

such that for a given Ln substitution level x , y is linearly related to the oxygen to metal ratio.

For “reduced” compositions which are fully charge compensated by oxygen vacancies ($y = 0$), Eq. 2 becomes

$$\Delta H_f = H[U_{1-x}\text{Ln}_x\text{O}_{2-0.5x}] - (1-x)H[\text{UO}_2] - xH[\text{LnO}_{1.5}] \quad (4)$$

and for stoichiometric compositions which are fully charge compensated by U^{5+} compensation ($y = 0.5x$), Eq. 2 becomes

$$\Delta H_f = H[U_{1-x}\text{Ln}_x\text{O}_2] - \left(1 - \frac{3x}{2}\right)H[\text{UO}_2] - xH[\text{LnO}_{1.5}] - \frac{x}{2}H[\text{UO}_3] \quad (5)$$

In Eq. 2, $H[\text{UO}_2]$ is for fluorite-structured UO_2 , and $H[\text{LnO}_{1.5}]$ is for Ln_2O_3 in the experimentally observed (i.e., room temperature) cubic bixbyite (C-type sesquioxide) or hexagonal (A-type) structure. Experimentally, Y_2O_3 is C-type, Nd_2O_3 exists in both C-type and A-type forms, and La_2O_3 is A-type [54]. In the calculations, all enthalpies are approximated by zero temperature total energies.

The calculated and experimental formation enthalpies (from Ln_2O_3 , UO_2 , and UO_3) for 1/2 and 1/3 Ln substitution levels where $\text{Ln}=\text{Y}$, Nd , and La are plotted against oxygen to metal

ratio (O/M) in Fig. 2. We find that the experimental data (denoted by filled circles), for compositions that are near-stoichiometric ($O/M = 2$) or hyperstoichiometric ($O/M > 2$) are highly exothermic and tend to show very little dependence on oxygen content in this regime.

In the hypostoichiometric ($O/M < 2$) regime, the calculated formation enthalpy (denoted by open circles) is most endothermic for fully oxygen vacancy compensated systems and becomes more exothermic with increasing oxygen content. The large energetic change with oxygen content in this regime compared to the minimal change in formation enthalpy for $O/M > 2$ can be attributed to different defect mechanisms in the two regimes. For $O/M < 2$, as the oxygen content increases, oxygen vacancies are filled and U^{4+} is oxidized to higher oxidation states; for $O/M > 2$, oxygen vacancies are not expected to contribute significantly to the energetics, and increasing oxygen content is accommodated primarily through the formation of oxygen interstitials and related defect clusters [26]. The computational results for $U_{1-x}Ln_xO_{2-0.5x}$ materials suggest their lack of stability (slightly positive ΔH_f), relative to the strongly stabilized stoichiometric $U_{1-x}Ln_xO_2$ materials. This difference may explain why it has been extremely difficult to prepare samples in the vacancy regime even with substantial rare earth doping as seen in ref. [18].

Next we make direct comparisons between calculation and experiment at similar oxygen compositions. Specifically, we compare the formation enthalpies with respect to Ln dopant cation size in Fig. 3. The compositions considered are fully stoichiometric ($O/M = 2$) with exactly one half or one third Ln substitution ($Ln/(Ln+U) = 0.5$ or 0.33). The experimental Ln substitution levels correspond exactly or are very close to the substitution levels used in the calculations. The calculations and experiments show agreement for all compositions within 10 kJ/mol. This level of agreement is viewed to be very satisfactory considering the influence on the

computed energetics of different approximations used in the first principles calculations. For example, in our previous work comparisons between formation energies computed with DFT+U and hybrid methods were reported Y and La doped UO_2 [19], with the hybrid functionals giving enthalpies of formation that were more exothermic by approximately 5 - 6 kJ/mol. The present comparisons between experiment and theory may suggest that the hybrid methods would lead to improved agreement with measurements, although further work would be needed at the stoichiometric oxygen concentrations to draw definitive conclusions.

The calculations allow us to look at systematic trends in the lattice parameter change with respect to fluorite UO_2 with for the various Ln dopant species and doping levels, as represented in Fig. 4 for stoichiometric oxygen to metal compositions. Fig. 4 shows that for all three Ln dopant species, increasing doping level gives rise to a greater lattice parameter mismatch, although this increase is the smallest for Ln = Nd. Furthermore, for Ln = Y, there is lattice contraction upon doping, whereas for the larger Nd and La cations, lattice expansion occurs. The largest lattice parameter mismatch occurs for Ln = Y, which is a possible explanation for why it is the least stable solid solution energetically. All these findings are qualitatively consistent with experimental observations [18].

4. Discussion of Trends in Oxygen Deficient Systems

In fluorite structured AO_2 compounds, with A=Hf, Zr, Ce, and Th, substitution of the host (A) cation with trivalent rare earths is observed to lead to the formation of charge-compensating oxygen vacancies [33]. In the limiting case where the oxygen/metal ratio corresponds to complete charge compensation by oxygen vacancies the host (A) remains primarily tetravalent and the defect chemistry can be described as follows:

Since experimentally it has proven difficult to prepare rare earth urania solid solution samples with the reduced $U_{1-x}Ln_xO_{2-0.5x}$ oxygen stoichiometries, first principles calculations will be used as a basis for comparing results for urania solid solutions with those in the related fluorite compounds based on tetravalent Zr, Hf, Ce and Th in this hypostoichiometric regime.

Specifically, we make direct comparison of the formation enthalpies (see Eq. 7) of $A_{1-x}Ln_xO_{2-0.5x}$ fluorite oxides from constituent oxides at the similar dopant levels with calorimetric and computational results in Fig. 5.

$$\Delta H_f = H[A_{1-x}Ln_xO_{2-0.5x}] - (1-x)H[AO_2] - xH[LnO_{1.5}] \quad (7)$$

As shown in Figs. 5a and 5b, the dopant concentrations selected for comparison are 1/3 and 1/2, which are the exact x value for calculations, and the same or very similar values for experiments. The radii of the tetravalent host cations ($A = \text{Hf, Zr, Ce, U, Th}$) and trivalent dopant cations ($Ln = \text{Yb, Y, Dy, Gd, Sm, Nd, La}$) in eightfold coordination are listed in Table 2. It should be noted here we are comparing the formation enthalpies of these doped fluorite oxides from fluorite AO_2 and $LnO_{1.5}$ in the cubic bixbyite (C-type sesquioxide) or hexagonal (A-type) structure, where $YbO_{1.5}$, $YO_{1.5}$, $DyO_{1.5}$, $GdO_{1.5}$, and $SmO_{1.5}$ are C-type sesquioxides, $NdO_{1.5}$ is dimorphic and $LaO_{1.5}$ is A-type [54]. Since neither ZrO_2 nor HfO_2 has the fluorite structure at room temperature, and the reported calorimetric formation enthalpies of doped zirconia and doped hafnia are from $LnO_{1.5}$ and monoclinic AO_2 [35], the energetics of their transformation to

fluorite structure needs to be accounted for. After such correction we obtain the formation enthalpies of $A_{1-x}Ln_xO_{2-0.5x}$ (A=Hf, Zr) that are shown in Fig. 5 by,

$$\Delta H_f = \Delta H_{f,ox}[A_{1-x}Ln_xO_{2-0.5x}] - (1-x)\Delta H_{trans}[AO_2] \quad (8)$$

The transformation enthalpies of HfO_2 and ZrO_2 from the monoclinic to cubic fluorite structure used here (8.8 ± 3.4 kJ/mol and 26 ± 1.0 kJ/mol respectively) are taken from Simocic and Navrotsky [34].

As displayed in Fig. 5, when trivalent dopant cation size increases, the formation enthalpies of different doped AO_2 fluorite oxides monotonically decrease, for a given fixed cation substitution level. Both the experimental and computational results display this stabilizing effect when adding larger trivalent dopants. Specifically, the computational data for doped urania and thoria show the decreasing formation enthalpies with increasing dopant radius, and a similar trend is shown in the experimental data for doped hafnia, zirconia, and ceria. Concomitantly, as the tetravalent host cation radius decreases (Fig. 6), the doped fluorite oxide becomes more energetically favorable. When direct comparisons can be made between calculations and experiments in Figs. 5 and 6, the enthalpies agree within 10 kJ/mol.

Next we combine what we learned from Figs. 5 and 6 to explore how size differences between the host and dopant cations affect the energetics. Instead of using the cation radii as the variables as shown in Figs. 5 and 6, here we introduce the relative size mismatch between the dopant (Ln^{3+}) and host (A^{4+}) cations,

$$\Delta r = abs(\frac{r_{A^{4+}} - r_{Ln^{3+}}}{r_{A^{4+}}}) \quad (9)$$

We redraw Fig. 5 by converting the x-axis of $r_{Ln^{3+}}$ to Δr , and thus obtain Fig. 7. Thereby we can compare all the doped fluorite oxide systems directly. The dashed lines shown in Fig. 7 are obtained by fitting the experimental calorimetric formation enthalpies.

As, Δr increases, ΔH_f decreases, leading to enhanced thermodynamic stability. As the size mismatch reaches 10 to 15 %, the formation enthalpy changes from slightly endothermic to increasingly exothermic. The computational results on doped ZrO_2 , UO_2 , and ThO_2 are consistent with the general trends seen in the experimental data. This change in energetics with size mismatch can be attributed to defect clustering tendencies for each doped fluorite oxide system. The enhanced stability of systems with larger size mismatch (i.e., smaller host A^{4+} cation, larger Ln^{3+} cation) is interpreted to be associated with a preference for reduced (increased) oxygen ion coordination of the host (dopant) cation [20]. Specifically, the formation of a fluorite-structured solid solution from AO_2 and Ln_2O_3 constituents necessarily leads to a decrease (increase) in the average oxygen coordination surrounding the A^{4+} (Ln^{3+}) cation, relative to the 8-fold (6-fold/7-fold) coordination characteristic of the pure AO_2 (Ln_2O_3). Therefore, systems with small host cations which prefer lower coordination (e.g., Zr^{4+} , Hf^{4+}) and large dopant cations which prefer higher coordination (e.g., Sm^{3+} , Nd^{3+} , La^{3+}) are expected to be more energetically favorable.

5. Conclusions

A combined experimental and computational investigation of the energetic properties of rare earth substituted UO_2 systems is presented, based on calorimetric measurements and DFT-based calculations. For compositions where direct comparisons between theory and experiment

are possible, agreement within 10 kJ/mol is obtained. Systematic trends based on previous experimental and computational thermochemical studies of rare earth substituted fluorite oxides with oxygen vacancy compensation, and results of the current work are presented. Consistent trends are found for all systems considered (including actinide and non-actinide oxide systems), demonstrating that larger size mismatch between the smaller host fluorite cation (A^{4+}) and the larger rare earth dopant cation (Ln^{3+}) gives rise to more energetically stable solid solutions. Substituted UO_2 is unique compared to the other substituted fluorite oxides considered, however, due to a strong energetic preference for higher oxygen compositions, regardless of the rare earth dopant species and doping level.

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Table. 1. The compositions considered for the calculations in this work are shown. The first through fifth columns represent the formula, number of U^{4+} ions, number of U^{5+} ions, number of oxygen vacancies, and number of symmetrically-distinct structures, respectively.

Formula	U^{4+}	U^{5+}	O_{vac}	Structures
Reduced				
$U_4Ln_2O_{11}$	4	0	1	117
$U_2Ln_2O_7$	2	0	1	27
Stoichiometric				
$U_4Ln_2O_{12}$	2	2	0	100
$U_2Ln_2O_8$	0	2	0	5
Intermediate				
$U_4Ln_4O_{15}$	2	2	1	7296

Table. 2. The cation sizes in eightfold coordination taken from ref. [55].

Tetravalent host cation (A^{4+})	$r_{A^{4+}}$ (Å)	Trivalent dopant cation (Ln^{3+})	$r_{Ln^{3+}}$ (Å)
Hf	0.83	Yb	0.985
Zr	0.84	Y	1.019
Ce	0.97	Dy	1.027
U	1.0	Gd	1.053
Th	1.05	Sm	1.079
-	-	Nd	1.109
-	-	La	1.16

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Fig. 1. The substitution of two U^{4+} by two Ln^{3+} can be charge compensated by one O_{vac} , or in more oxidizing environments, charge compensation can occur by oxidation of U^{4+} to U^{5+} for every one Ln^{3+}/U^{4+} substitution, as illustrated in the motifs above. Systems with compositions that are intermediate between fully oxygen vacancy charge-compensated and fully U^{5+} charge-compensated contain both oxygen vacancies and U^{5+} ions.

Fig. 2. Formation enthalpies (ΔH_f) of $U_{1-x}Ln_xO_{2-0.5x+y}$ structures are shown for the calculated lowest-energy fully relaxed structures of all compositions enumerated in this study, in comparison to calorimetric data presented previously [18]. The enthalpies are plotted against oxygen-to-metal ratio (O/M), which is related to x and y according to Eq. 3.

Fig. 3. The formation enthalpies calculated for stoichiometric compositions for both calculation (“Comp.”) and experiment (“Exp.”) with respect to Ln dopant cation size are shown.

Fig. 4. The first-principles calculated percent lattice parameter difference relative to fluorite UO_2 for the three Ln dopant species considered in this work for stoichiometric compositions with $x=1/3$ and $1/2$ doping levels are shown.

Fig. 5. Formation enthalpies of $A_{1-x}Ln_xO_{2-0.5x}$ fluorite oxides from $LnO_{1.5}$ and fluorite AO_2 from calorimetric and computational results, as a function of trivalent dopant cation radius, where $x = 1/3$ in Fig. 5a and $x = 1/2$ in Fig. 5b.

^aLee and Navrotsky [29] ^bSimoncic and Navrotsky [35] ^cSimoncic and Navrotsky [34] ^dBogicevic et al. [27] ^eChen et al. [30] ^fNavrotsky et al. [31] ^gBuyukkilic et al. [32] ^hSolomon et al. [19] ⁱThis work ^jAizenshtein et al. [33] ^kAlexandrov et al. [28] ^lSolomon et al. [20]

Fig. 6. Formation enthalpies of $A_{1-x}Ln_xO_{2-0.5x}$ fluorite oxides ($x=1/3, 1/2$) from $LnO_{1.5}$ and fluorite AO_2 from calorimetric and computational results, as a function of tetravalent host cation radius, where $Ln = Y$ in Fig. 6a, $Ln = Gd$ in Fig. 6b, and $Ln = La$ in Fig. 6c. Redrawn from data in Fig. 5.

Fig. 7. Formation enthalpies of $A_{1-x}Ln_xO_{2-0.5x}$ fluorite oxides from $LnO_{1.5}$ and fluorite AO_2 from calorimetric and computational results, as a function of size mismatch of trivalent dopant and tetravalent host cations, where $x = 1/3$ in Fig. 7a and $x = 1/2$ in Fig. 7b. Redrawn from data in Fig. 5. The dashed lines shown in the figure are obtained by fitting only the experimental data.

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7