Acta Materialia 97 (2015) 191–198

Contents lists available at ScienceDirect

Acta Materialia

journal homepage: www.elsevier.com/locate/actamat

A combined calorimetric and computational study of the energetics of rare earth substituted UO_2 systems

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ARTICLE INFO

Article history:
Received 24 March 2015
Accepted 20 June 2015
Available online 13 July 2015

Keywords:
Formation enthalpy
Fluorite oxide
Calorimetry
DFT

ABSTRACT

The energetics of rare earth substituted UO_2 solid solutions ($U_{1-x}Ln_xO_{2-0.5x+y}$, 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 ($A_{1-x}Ln_xO_{2-0.5x}$, 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.

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 [14–16] 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 [17,18]. 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 $Ln_xU_{1-x}O_{2-0.5x+y}$ 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 relatively recently [19,20]. 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 [21,22]. In the present work the computational studies are extended to consider compositions with oxygen stoichiometries varying from the limit of oxygen vacancy

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http://dx.doi.org/10.1016/j.actamat.2015.06.048
1359-6454/

compensation up to stoichiometric oxygen/metal ratios. We note that, due to the importance of oxygen clustering at hyperstoichiometric compositions [23–26], 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 [19,20,27,28] and experimental [29–35] 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 ($Ln_xU_{1-x}O_{2-0.5x+y}$, where Ln = La, 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 ($3NaO \cdot 4MoO_3$) 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 by the structural motifs 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) [37,38]. 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

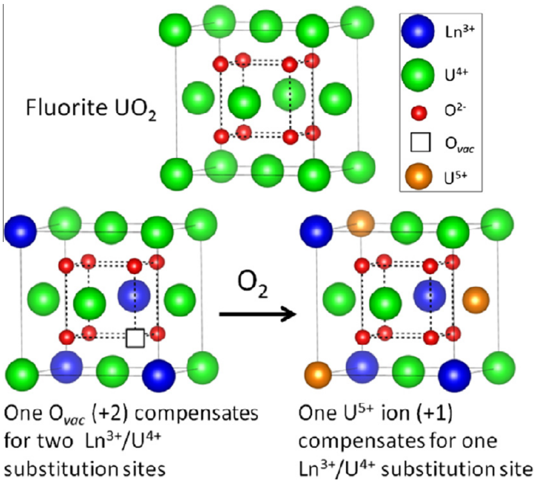

Fig. 1. The substitution of two U^{4+} by two Ln^{3+} can be charge compensated by one O_{vac}, or in more oxidizing environments, charge compensation can occur by oxidation of U^{4+} to U^{5+} for every one Ln^{3+}/U^{4+} substitution, as illustrated in the motifs above. Systems with compositions that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