



# Thermochemistry of $\text{UO}_2 - \text{ThO}_2$ and $\text{UO}_2 - \text{ZrO}_2$ fluorite solid solutions



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## ABSTRACT

The enthalpies of formation of cubic urania – thoria ( $c\text{-Th}_x\text{U}_{1-x}\text{O}_{2+y}$ ) and urania – zirconia ( $c\text{-Zr}_x\text{U}_{1-x}\text{O}_2$ ,  $x < 0.3$ ) solid solutions at 25 °C from end-member binary oxides ( $c\text{-UO}_2$ , and  $c\text{-ThO}_2$  or  $m\text{-ZrO}_2$ ) have been measured by high temperature oxide melt solution calorimetry. The enthalpies of mixing for both systems are zero within experimental error. The interaction parameters for binary solid solutions  $\text{MO}_2 - \text{M}'\text{O}_2$  ( $\text{M}, \text{M}' = \text{U}, \text{Th}, \text{Ce}, \text{Zr}, \text{and Hf}$ ), fitted by regular and subregular thermodynamic models using both calorimetric and computational data, increase linearly with the corresponding volume mismatch. Cubic  $\text{UO}_2 - \text{ZrO}_2$  appears to be an exception to this correlation and shows a zero heat of mixing despite large size mismatch, suggestive of some short-range ordering and/or incipient phase separation to mitigate the strain. The incorporation of  $\text{ZrO}_2$  into  $\text{UO}_2$  stabilizes the system and makes it a potential candidate for immobilization and disposal of nuclear waste.

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## 1. Introduction

Uranium dioxide forms fluorite-structured solid solutions with a variety of di-, tri- and tetravalent cations [1–3]. Many factors affect the incorporation of cations into  $\text{UO}_2$ , including ion size, charge, and oxidation states and ability of the substituent oxide to form the fluorite structure separately [4]. Understanding the energetic penalties or benefits associated with this process is crucial because it is relevant to the nuclear fuel cycle, including the development of proliferation-resistant fuel and the management of waste forms and products of reactor accidents [5–7].

Thoria-based nuclear fuel offers advantages in increasing burn-up and lowering amounts of minor actinides [8,9]. Also, the incorporation of Th into  $\text{UO}_2$  greatly decreases its solubility and dissolution rate in aqueous environments [10–12], thus providing additional stability to the waste form for direct disposal of spent nuclear fuel.  $\text{ThO}_2$  and  $\text{UO}_2$  form continuous solid solutions and maintain the cubic fluorite structure due to their close ionic sizes [13]. Their oxidation and thermodynamic properties have been studied [14,15], where solid solutions rich in U remain in the fluorite structure even with the incorporation of oxygen interstitials.

Urania-zirconia solid solutions are expected to improve the chemical stability and radiation resistance of fuel pellets and hence are of great interest for immobilization and disposal of spent nuclear fuel [16]. Moreover, “corium”, mainly  $\text{UO}_2 - \text{ZrO}_2$  solution,

forms at temperatures above 2500 °C during a severe loss of coolant accident in light water pressurized reactor [17]. Unlike  $\text{ThO}_2$ ,  $\text{ZrO}_2$  has polymorphs that are more stable than the fluorite structure at lower temperatures (monoclinic zirconia is stable up to 1160 °C, tetragonal zirconia is stable up to 2370 °C, and cubic zirconia is stable up to its melting point at 2680 °C [18]). As study on the  $\text{UO}_2 - \text{ZrO}_2$  phase diagram has shown [19], up to 30 mol%  $\text{ZrO}_2$  can be incorporated into  $\text{UO}_2$  while retaining the fluorite structure.

While studies have been performed on the heat capacity and solubility of  $\text{ThO}_2$  and  $\text{ZrO}_2$  in fluorite structured  $\text{UO}_2$  [15,19–21], experimental measurements of formation and mixing enthalpies of such solid solutions have not been reported. Theoretical study of the thermochemical properties of  $\text{Th}_x\text{U}_{1-x}\text{O}_2$  predicts its mixing enthalpy to be slightly positive [22,23]. In this paper we report the first direct measurements of enthalpies of mixing for  $\text{UO}_2 - \text{ThO}_2$  and  $\text{UO}_2 - \text{ZrO}_2$  solid solutions by high temperature oxide melt solution calorimetry. We also substantiate a linear correlation of interaction parameters and volume mismatch for fluorite oxide solid solution systems.

## 2. Experimental procedures

### 2.1. Syntheses

A co-precipitation method (utilized for other  $\text{UO}_2$  – based fluorite solid solutions [2,24,25]) was used to synthesize samples of  $\text{Th}_x\text{U}_{1-x}\text{O}_{2+y}$  solid solutions containing 22, 43, and 75 mol%  $\text{ThO}_2$

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and  $Zr_xU_{1-x}O_2$  solid solutions containing 8, 16, and 29 mol%  $ZrO_2$ . Corresponding amounts of  $UO_2(NO_3)_2 \cdot 6H_2O$  and  $Th(NO_3)_4 \cdot 5H_2O / ZrO(NO_3)_2 \cdot H_2O$  (all Sigma-Aldrich with metal purity 98–99%) were dissolved in 30 ml of deionized water in a Teflon beaker. After dissolution, the pH of the solution was raised to 10 by adding  $NH_4OH$ . Precipitates formed immediately, and the solution was transferred to a platinum crucible and dried in an oven at 150 °C overnight. The remaining sample powders were further calcined at 800 °C for 6 h. Afterwards samples were ground, placed in alumina boats, and heated in a tube furnace by two different procedures. First, hyperstoichiometric samples ( $Th_xU_{1-x}O_{2+y}$ ) were achieved by heating the calcined powders in an Ar/5%  $H_2$  (v/v) atmosphere at 1400 °C for 70 h, cooling to 850 °C at 5 °C·min<sup>-1</sup>, and removing from the furnace. Second, stoichiometric samples of both  $Zr_xU_{1-x}O_2$  and  $Th_xU_{1-x}O_2$  were obtained by further heating the hyperstoichiometric samples in a stream of Ar at 1400 °C for 48 h, followed by regrinding and heating in Ar/5%  $H_2$  (v/v) atmosphere at 1400 °C for 10 h. These samples were cooled to room temperature at 5 °C·min<sup>-1</sup> before being taken out of the furnace.

## 2.2. Characterization

Synthesized samples were characterized by various techniques to verify their structure, phase purity, and composition. Phases present and their lattice parameters were determined by powder X-ray diffraction (PXRD) measurements by a Bruker D-8 Advance

diffractometer using Cu  $K_\alpha$  radiation, a step size of 0.02 °2 $\theta$ , and whole pattern refinement. The homogeneity of each sample was confirmed by electron probe microanalysis (EPMA) with wavelength dispersive spectroscopy (WDS) by Cameca SX-100. Ten randomly located points, 1  $\mu$ m in diameter, were analyzed for each sample for their composition and averaged to confirm a homogeneous phase with no secondary phases, using standards  $ThO_2$  for Th ( $M_\alpha$  line),  $ZrO_2$  for Zr ( $L_\alpha$  line), and  $UO_2$  for U ( $M_\alpha$  line). The metal ratios of the samples (Th/U mol% and Zr/U mol%) were also measured.

For the stoichiometric  $Th_xU_{1-x}O_2$  and  $Zr_xU_{1-x}O_2$  solid solutions, uranium oxidation states were measured by XANES done at the Advanced Photon Source at Argonne National Laboratory by comparing relative shifts of U L<sub>III</sub>-edge in the samples and  $UO_2$  standard. To completely determine the compositions of hyperstoichiometric  $Th_xU_{1-x}O_{2+y}$  solid solutions, their oxygen contents were measured by a titration method that was developed for doped uranium oxides [2].  $Th_xU_{1-x}O_{2+y}$  samples (20–30 mg) were dissolved in 5 mL of 0.05 mol·L<sup>-1</sup> cerium (IV) sulfate solution with sulfuric acid and concentrated phosphoric acid while heating and bubbling  $N_2$ . After complete dissolution of the oxides where U(IV) was oxidized to U(VI) only by Ce(IV), the amount of Ce(IV) remaining was determined by back-titration with Fe(II) solutions. Hence the uranium oxidation states and oxygen stoichiometry were determined. All the chemicals used in this study are described in Table 1.

## 2.3. Calorimetry

The enthalpies of drop solution of the  $UO_2 - ThO_2$  and  $UO_2 - ZrO_2$  solid solutions into molten lead borate ( $2PbO \cdot B_2O_3$ , Viox Inc., >99%) at 800 °C were measured in a custom built Tian-Calvet high-temperature microcalorimeter [26–28], and the enthalpies of formation for each system were calculated by thermochemical cycles as listed in Tables 2 and 3. Oxide samples were ground, and about 7 mg of the powders were pressed into a small pellet with 1.6 mm in diameter. The pellet was measured in microbalance and dropped from room temperature into 30 g of molten oxide solvent contained in the Pt crucibles in the calorimeter. To facilitate the dissolution of the refractory oxide sample and oxidize the uranium to the hexavalent state, oxygen gas was flushed through the calorimetric assembly at 70 mL/min and bubbled in the molten solvent at 5 mL/min. While the  $Zr_xU_{1-x}O_2$  and  $Th_xU_{1-x}O_2$  samples are stoichiometric, their formation enthalpies from end-member oxides are calculated. The  $Th_xU_{1-x}O_{2+y}$  samples are hyperstoichiometric; thus the formation enthalpies from  $ThO_2$ ,  $UO_2$ , and  $UO_3$  or  $O_2$  are calculated respectively.

## 3. Results and discussion

The samples used in this study are homogeneous single-phase materials with cubic fluorite structure as characterized by EPMA

**Table 1**  
List of samples and compounds used.

Composition	Source	Purity (%)	Analysis method
$Th_{0.22}U_{0.78}O_{2.32}$	Synthesis	>98	XRD, EPMA
$Th_{0.43}U_{0.57}O_{2.23}$	Synthesis	>98	XRD, EPMA
$Th_{0.75}U_{0.25}O_{2.09}$	Synthesis	>98	XRD, EPMA
$Th_{0.22}U_{0.78}O_2$	Synthesis	>98	XRD, EPMA
$Th_{0.43}U_{0.57}O_2$	Synthesis	>98	XRD, EPMA
$Th_{0.75}U_{0.25}O_2$	Synthesis	>98	XRD, EPMA
$Zr_{0.08}U_{0.92}O_2$	Synthesis	>98	XRD, EPMA
$Zr_{0.16}U_{0.84}O_2$	Synthesis	>98	XRD, EPMA
$Zr_{0.29}U_{0.71}O_2$	Synthesis	>98	XRD, EPMA
$Th(NO_3)_4 \cdot 5H_2O$	Sigma-Aldrich	99.9	Manufacturer ICP, checked with PXRD
$ZrO(NO_3)_2 \cdot H_2O$	Sigma-Aldrich	99.9	Manufacturer ICP, checked with PXRD
$UO_2(NO_3)_2 \cdot 6H_2O$	Sigma-Aldrich	99.9	Manufacturer ICP, checked with PXRD
Deionized $H_2O$	Millipore	99.99	ICP
$NH_4OH$	Sigma-Aldrich	99.9	Manufacturer ICP
$H_2SO_4$	Alfa Aesar	95–98	Manufacturer ICP
$Ce(SO_4)_2$	Fluka Analytical	99.9	Manufacturer ICP
$FeSO_4$	Fischer	99.9	Manufacturer ICP
$MoO_3$	Fischer	99.5	Manufacturer ICP, checked with PXRD
$NaMoO_4 \cdot 2H_2O$	EMD Millipore	99.5	Manufacturer ICP, checked with PXRD

**Table 2**  
Reactions and thermodynamic cycles used to calculate enthalpies of formation of the fluorite phase  $Th_xU_{1-x}O_{2+y}$  at 25 °C from oxides with respect to  $ThO_2$  and  $UO_2$  with fluorite structure, and  $UO_3$  or oxygen.

Reaction	Enthalpy of the reaction (kJ·mol <sup>-1</sup> )
(1) $Th_xU_{1-x}O_{2+y}$ (fluorite, 25 °C) + $0.5(1-x-y)O_2$ (g, 800 °C) → $xThO_2$ (soln, 800 °C) + $(1-x)UO_3$ (soln, 800 °C)	$\Delta H_1 = \Delta H_{DS}$
(2) $ThO_2$ (fluorite, 25 °C) → $ThO_2$ (soln, 800 °C)	$\Delta H_2 = 98.1 \pm 1.7$ [43]
(3) $UO_2$ (fluorite, 25 °C) + $0.5O_2$ (g, 800 °C) → $UO_3$ (soln, 800 °C)	$\Delta H_3 = -125.21 \pm 3.41$ [44]
(4) $UO_3$ (25 °C) → $UO_3$ (soln, 800 °C)	$\Delta H_4 = 26.67 \pm 4.02$ [44]
(5) $O_2$ (g, 25 °C) → $O_2$ (g, 800 °C)	$\Delta H_5 = 25.4$ [32]
(6) $xThO_2$ (fluorite, 25 °C) + $(1-x-y)UO_2$ (fluorite, 25 °C) + $yUO_3$ (25 °C) → $Th_xU_{1-x}O_{2+y}$ (fluorite, 25 °C)	$\Delta H_6 = \Delta H_{f,ox}$
(7) $xThO_2$ (fluorite, 25 °C) + $(1-x)UO_2$ (fluorite, 25 °C) + $0.5yO_2$ (25 °C) → $Th_xU_{1-x}O_{2+y}$ (fluorite, 25 °C)	$\Delta H_7 = \Delta H_{f,ox+oxygen}$
$\Delta H_6 = -\Delta H_1 + x\Delta H_2 + (1-x-y)\Delta H_3 + y\Delta H_4$	
$\Delta H_7 = -\Delta H_1 + x\Delta H_2 + (1-x)\Delta H_3 + 0.5y\Delta H_5$	
When $y = 0$ , $\Delta H_6 = \Delta H_{f,ox} = \Delta H_{mix} = -\Delta H_1 + x\Delta H_2 + (1-x)\Delta H_3$	

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