

Charge distribution and local structure and speciation in the UO_{2+x} and PuO_{2+x} binary oxides for $x \leq 0.25$

Steven D. Conradson^{a,*}, Bruce D. Begg^b, David L. Clark^a, Christophe den Auwer^c, Mei Ding^a, Peter K. Dorhout^d, Francisco J. Espinosa-Faller^{a,e}, Pamela L. Gordon^a, Richard G. Haire^f, Nancy J. Hess^g, Ryan F. Hess^a, D. Webster Keogh^a, Gerard H. Lander^h, Dario Manara^h, Luis A. Morales^a, Mary P. Neu^a, Patricia Paviet-Hartmann^a, Jean Rebizant^h, Vincenzo V. Rondinella^h, Wolfgang Runde^a, C. Drew Tait^a, D. Kirk Veirs^a, Phillip M. Villella^a, Franck Wastin^h

^aLos Alamos National Laboratory, Chemistry Division, Materials Science and Technology Division and Nuclear Materials Technology Division, Los Alamos, NM 87545, USA

^bAustralian Nuclear Science and Technology Organisation, Menai, NSW 2234, Australia

^cCommissariat à l'Energie Atomique, Marcoule, 30207 Bagnols sur Ceze Cedex, France

^dColorado State University, Fort Collins, CO 80523, USA

^eCentro Marista de Estudios Superiores, Merida, Yucatan, Mexico

^fOak Ridge National Laboratory, Oak Ridge, TN 37831, USA

^gPacific Northwest National Laboratory, Richland, WA 99352, USA

^hEuropean Commission, JRC, Institute for Transuranium Elements, D-76125 Karlsruhe, Germany

Received 3 June 2004; received in revised form 10 September 2004; accepted 16 September 2004

Abstract

The local structure and chemical speciation of the mixed valence, fluorite-based oxides UO_{2+x} ($0.00 \leq x \leq 0.20$) and $\text{PuO}_{2+x}/\text{PuO}_{2+x-y}(\text{OH})_{2y} \cdot z\text{H}_2\text{O}$ have been determined by U/Pu L_{III} XAFS spectroscopy. The U spectra indicate (1) that the O atoms are incorporated as oxo groups at short (1.75 Å) U–O distances consistent with U(VI) concomitant with a large range of U displacements that reduce the apparent number of U neighbors and (2) that the UO_2 fraction remains intact implying that these O defects interact to form clusters and give the heterogeneous structure consistent with the diffraction patterns. The PuO_{2+x} system, which does not show a separate phase at its $x = 0.25$ endpoint, also displays (1) oxo groups at longer 1.9 Å distances consistent with $\text{Pu(V} + \delta)$, (2) a multisite Pu–O distribution even when x is close to zero indicative of the formation of stable species with H_2O and its hydrolysis products with O^{2-} , and (3) a highly disordered, spectroscopically invisible Pu–Pu component. The structure and bonding in AnO_{2+x} are therefore more complicated than have previously been assumed and show both similarities but also distinct differences among the different elements.

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Keywords: Speciation; Local structure; X-ray absorption fine structure spectroscopy; Urania; Plutonia; Mixed valence actinide oxide; XAFS

1. Introduction

Crystallographically, i.e., based on their diffraction patterns that originate in the long-range average

arrangement of atoms contained in the coherent parts of the crystal, the AnO_2 compounds display the fluorite structure for Pa–Cf [1]. In this, the O^{2-} ions form a lattice of cubes in which alternating cube-centers are occupied by the An(IV) ions. Each An(IV) is therefore surrounded by a cube of O^{2-} and the nearest neighbor environment for every O^{2-} is a tetrahedron of An(IV)

*Corresponding author. Fax: +1 505 665 8021.

E-mail address: conradson@lanl.gov (S.D. Conradson).

ions. The structures of these compounds are therefore relatively open and their densities relatively low because half of the cubes are empty.

If the AnO_2 compounds were inert and truly stable then not only would the technical issues involving them be easily resolved but they also would be of little scientific interest [2]. This is, however, not the case. Especially, when prepared from solution, many An ions in AnO_2 -type materials coordinate OH^- ions (and possibly H_2O) that are only slowly expelled as the materials consolidate [3,4]. In addition, at least UO_2 , [5] NpO_2 , [6–9] and PuO_2 [10] are readily oxidized (and reduced) with concomitant addition (loss) of O atoms from the lattice [1]. In fact, x can be varied continuously over a range specific to each element, from as low as -0.5 (Pu) to $+1$ (U). The valence endpoint and most stable phase are highest for U and lowest for Pu, one manifestation of which is the fact that UO_2 readily oxidizes to higher forms in air whereas PuO_2 does not. AnO_2 may therefore often best be described as $\text{AnO}_{2\pm x}$, or even $\text{AnO}_{2+x-y}(\text{OH})_{2y} \cdot z\text{H}_2\text{O}$. One of the more remarkable aspects of this behavior is that the basic crystallographic structure is mostly conserved for $-0.5 \leq x \leq 0.5$ and beyond. Even as O atoms are added or removed, the diffraction pattern from the cubic An sublattice is retained except for changes of a few hundredths of an Å in its lattice constant that are the only indication the formation of the new, isostructural phases. For example, Pu_2O_3 is produced from PuO_2 by the sequential removal of every fourth O atom from the lattice. Similarly, 16 (or more) distinct phases have been identified between UO_2 and UO_3 that are all believed to be distinguished primarily by different, ordered arrangements of the O atoms that are (at lower x) adventitious to the original UO_2 structure, even while the U atoms undergo only minor displacements that conserve their symmetry [5]. Because of the stability of these putative phases relative to a random distribution of the extra O atoms or vacancies within the crystal, as oxidation occurs they form as clusters that coexist in the crystal with the original phase and grow and coalesce as the An:O ratio approaches the actual stoichiometry of the phase.

Based on both X-ray and neutron diffraction data, highly detailed descriptions of these phases and the structural mechanisms for their interconversions with the addition or loss of O atoms have been described for the UO_{2+x} system. The salient attribute of these mechanisms is that, consistent with the conservation of the U sublattice, the adventitious O atoms add through distortions and rearrangements of the O sublattice that tend to utilize the empty space of the unoccupied cubic sites. There is a long history for these models for UO_{2+x} $x \leq 0.25$, beginning with the “2:2:2” and “4:3:2” (referring to, respectively, O site vacancies and the numbers of O atoms displaced in [110] directions within

chains and [111] directions that terminate chains)-type defects and chains [11–14] and more recently progressing to more extended clusters involving cuboctahedral, antiprism-type distortions of the original cubes [5,15,16]. The additional charge on the U ions in these models therefore tends to be somewhat dispersed rather than localized and is accommodated by small (<0.15 Å) reductions in some U–O bond lengths (balanced by expansions of others) and increases in the U coordination numbers. There are, however, three problems with these models, that most likely originate in the fact that diffraction is sensitive to the periodic components of the structure whereas local structure probes such as X-ray absorption fine structure (XAFS) spectroscopy and pair distribution function analysis see all of the atoms [17]. Conceptually, this delocalized charge distribution is inconsistent with both the known molecular and actinate [18–21] chemistry of the lighter actinides. In the former, the higher An valences exhibit multiply bound “oxo” groups at very short (<1.85 Å) An–O distances and lower total coordination numbers. In the latter, higher An charge is also stabilized with fewer O near neighbors and contracted bonds that may be divided into sets of longer and shorter ones [20–22] or be totally symmetric, e.g., KUO_3 , [23] BaUO_4 , [24] Ba_3UO_6 [19]. In this regard it is worth noting that while U_2O_5 and Np_2O_5 both have oxo groups (albeit bridging), the former compound has not been identified as an intermediate in the UO_2 – UO_3 sequence but must be prepared by a different route [5]. Secondly, it is very difficult to determine the correct structures of disordered solids from diffraction data and the solutions to the fits of these patterns tend to be non-unique. Finally, whereas the oxidation of U and Np progress, respectively, to U(VI) and Np(V), PuO_{2+x} ceases oxidation at $x = 0.25$ without exhibiting a separate phase that would account for the stability of this stoichiometry. This contradicts the tenet of thermodynamics that holds that a disordered material should not be a minimum in the total free energy surface.

Knowing the mechanism by which the O atoms are added and removed is essential because it is required for understanding and predicting the behavior of these materials. For example, the original description of PuO_{2+x} was accompanied by the speculation that the presence of the Pu(V) in PuO_2 would increase the solubility of this environmentally critical compound. Likewise, corrosion (and other chemical reaction) rates and their sensitivities to the presence of contaminants also depend on the intermediates that occur between the reactants and products. Fortunately, a direct probe for the chemical speciation and local structure of the An in $\text{AnO}_{2+x-y}(\text{OH})_{2y} \cdot z\text{H}_2\text{O}$ independent of its long range order is available: XAFS spectroscopy [3,4,25,26]. This method has recently been used to characterize PuO_{2+x} [27–29] and UO_{2+x} [30] for $0.0 \leq x \leq 0.25$.

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