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U and Pu L_{iii} XAFS of Pu-doped glass and ceramic waste forms

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Abstract

X-Ray Absorption Fine Structure (XAFS) spectroscopic studies were performed on a suite of compositionally identical Pu-doped simulated waste glasses prepared 15 years ago at different α-activities by varying the $^{239}Pu/^{238}Pu$ isotopic ratio. The resulting α-activities range from 1.9×10^{7} to 4.2×10^{9} Bq g^{-1}. These samples have a current, accumulated dose that ranges from 8.8×10^{15} to 1.9×10^{18} α-decays g^{-1}. A second suite of polycrystalline zircon samples that were synthesized 16 years ago with 10.0 wt.% Pu was also investigated. The $^{239}Pu/^{238}Pu$ isotopic ratio in these samples resulted in α-activities of 2.5×10^{8} and 5.6×10^{10} Bq g^{-1} and an accumulated dose of 1.2×10^{17} and 2.8×10^{19} α-decays g^{-1}. For both the glass and ceramic waste forms, initial analysis of Extended X-Ray Absorption Fine Structure (EXAFS) and X-Ray Absorption Near Edge Structure (XANES) indicate that the local environment around the actinides exhibit different degrees of disorder as a result of the accumulated α-decay dose. © 1998 Published by Elsevier Science S.A.

Keywords: Radiation damage; X-Ray absorption spectroscopy; High-level radioactive waste glass

1. Introduction

Waste forms currently under consideration for permanent deposition of radioactive high level waste include lanthanide borosilicate glass and ceramic hosts. The radiation effects on the stability and durability of these waste forms has been actively pursued and yet there is still a lack of basic understanding on the radiation-damage process. As a result, the extrapolation of the limited understanding of damage accumulation to highly radioactive waste forms, such as that generated by HLW processing or the deposition of weapons-grade plutonium, leaves many scientists feeling uneasy about the conclusions based on these extrapolations. The samples studied here include a suite of aged borosilicate glasses in which the accumulated α-decay dose varies by a factor of 200 and a suite of plutonium-doped polycrystalline zircon samples which range from fully crystalline to amorphous by α-decay. The significance of these samples is that the cumulative α-decay doses of these samples are within the range calculated for proposed waste forms containing weapons-grade plutonium. At this time, no other aged samples with doses within this range have been studied in detail, particularly structural changes at the molecular level.

XAFS is ideally suited technique to address the effects of accumulated α-decay dose including changes in the oxidation state, local coordination and bonding of the parent actinides (e.g. ^{239}Pu) and their daughter products (e.g. ^{235}U) within the glass and ceramic waste forms. XAFS is sensitive to the changes in short range order that accompany the effects of radiation damage. Determination of the actinide and daughter product oxidation state is addressed using XANES spectroscopy. Analysis of the EXAFS spectra provides description of the coordination environments of the parent actinides, their daughter products, and host.

2. Experimental

The borosilicate glass used in this study is a reference defense waste glass with the composition given in Table 1.

Table 1
Composition of simulated waste glass

Oxide	Weight %	Oxide	Weight %	Oxide	Weight %
SiO_2	50.6	Li_2O_3	4.9	SrO	0.5
B_2O_3	7.0	MgO	0.7	ZrO_2	0.7
Al_2O_3	6.0	MnO_2	3.0	Cs_2O	0.5
CaO	2.0	Na_2O	9.1	U_3O_8	3.0
Fe_2O_3	10.0	NiO	2.0	PuO_2	1.0

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Table 2
Sample isotopic composition and accumulated α-decay dose

sample	Pu isotopic composition	accumulated dose (α-decays g^{-1})
DRG-P1	1.0 wt% $^{239}PuO_2$	8.8×10^{15}
DRG-P2	0.9 wt% $^{239}PuO_2$, 0.1 wt% $^{238}PuO_2$	2.0×10^{17}
DRG-P3	1.0 wt% $^{238}PuO_2$	1.9×10^{18}
^{239}Pu-doped zircon	10.0 wt% ^{239}Pu	1.2×10^{17}
^{238}Pu-doped zircon	8.85 wt% ^{238}Pu, 1.15 wt% ^{239}Pu	2.8×10^{19}

Three compositionally identical glass samples of this composition were prepared in July 1982 with 1 wt.% PuO_2 in which the $^{238}Pu/^{239}Pu$ isotopic composition of plutonium was varied resulting in a factor of 200 variation in the accumulated dose [1]. The zircon samples were prepared in August 1981 in which 8.1 mole% of zirconium was replaced by ^{239}Pu or ^{238}Pu [2]. The accumulated α-decay dose for these samples is given in Table 2.

XAFS measurements were conducted at the Stanford Synchrotron Radiation Laboratory on endstation 4-2 under dedicated operating conditions. Spectra were collected at the Pu and UL_{III}-edges in fluorescence mode at 77 K. The fluorescence signal was collected using a 13-element Ge detector. The phase and amplitude for the cation–oxygen and cation–silicon scattering paths were calculated using the ab initio code FEFF 7.02 [3,4]. The individual scattering paths were then parameterized and used to curvefit the EXAFS. The crystalline silicates coffinite ($USiO_4$), and $PuSiO_4$ were used to approximate the local cation environment in the waste glass. In addition, the uranium triscarbonato complex was used as the model for the dioxo- or 'yl' moiety and for the multiple scattering contributions, labeled U-O_{yl} and U-ms, respectively.

3. Results

Waste Glass. The XANES of the waste glass samples are shown as insets in Fig. 1. The absorption edge energy in the XANES readily indicates the oxidation state of elements. This particularly useful for elements with multiple oxidation states. At the U L_{III}-edge, all the waste glass samples exhibit the shoulder peak typical of 'yl' formation. The uranium absorption edge for all the samples fall at an energy range that is consistent with U^{4+}. Previous studies of uranium in waste glass have observed similar shoulder features and a shift of the absorption edge to lower energies than expected for U^{6+} [5–9]. In these studies, analysis of the U L_{III}-edge EXAFS revealed a distribution of bond lengths that is intermediate between the short U–O bond lengths typical of U^{4+} compounds and the longer equatorial U–O bond lengths characteristic of U^{6+}. In this intermediate environment it appears that the position of the absorption edge is influenced by the coordination environment around uranium in addition to its formal oxidation state. The DRG-P2 and DRG-P3 glasses exhibit a decrease in the height of the 'yl' shoulder peak suggesting that the amount of U^{6+} present in these glasses is less than that in

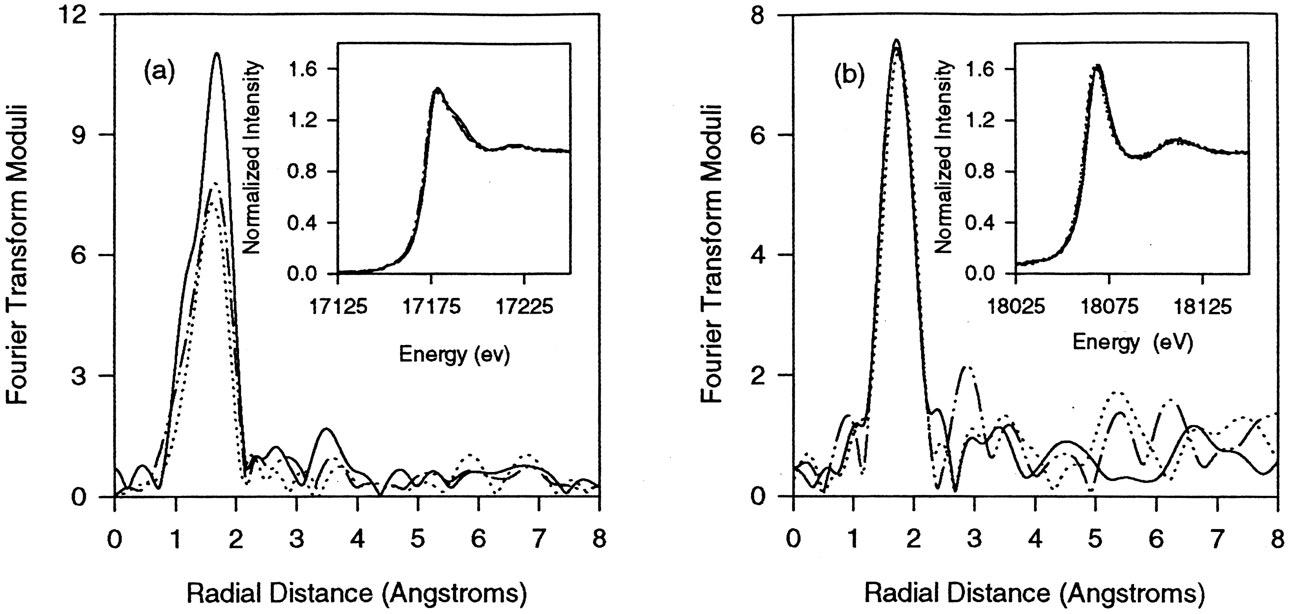

Fig. 1. The Fourier transform of the EXAFS of the Pu-doped waste glass at (a) the U L_{III}-edge, and (b) the Pu L_{III}-edge. XANES, are shown in inset. The solid line is DRG-P1, the dashed line is DRG-P2, and the dotted line is DRG-P3.

Table 3
EXAFS fitting results for waste glass

U L_{III}-edge	U–O_{yl}	U–O_{eq}	U–O	U–ms	U–U	
DRG-P1	distance	1.83±0.02	2.21±0.02	2.74±0.03	3.50±0.03	3.62±0.02
	number	1.8±0.5	5.7±0.4	1.9±0.6	1.1±0.3	1.9±0.5
r^2=0.7053	sigma	0. 01, fixed	0.08, fixed	0.10, fixed	0.02±0.07	0.07±0.02
DRG-P2	distance	1.79±0.02	2.24±0.02		3.51±0.03	
	number	1.1±0.3	4.5±1.2		2.9±0.9	
r^2=0.8169	sigma	0. 01, fixed	0.08, fixed		0.08±0.03	
DRG-P3	distance	1.80±0.02	2.22±0.02		3.50±0.04	
	number	1.0±0.3	3.7±1.0		1.7±0.5	
r^2=0.6958	sigma	0.01, fixed	0.08, fixed		0.10±0.03	
Pu L_{III}-edge			Pu–O		Pu–Si	
DRG-P1	distance		2.23±0.02		3.11±0.02	
	number		6.7±1.8		0.3±0.1	
r^2=1.0735	sigma		0.09, fixed		0.00±0.00	
DRG-P2	distance		2.23±0.03		3.05±0.02	
	number		6.0±1.7		0.9±0.3	
r^2=1.4705	sigma		0.09, fixed		0.00±0.00	
DRG-P3	distance		2.23±0.03		2.98±0.02	
	number		6.3±1.8		0.4±0.1	
r^2=1.6962	sigma		0.09, fixed		0.00±0.04	

the DRG-P1 sample. Plutonium is present as Pu^{4+}.

Analysis of the U L_{III}-edge EXAFS reveal a decrease in the number of 'yl' oxygens at approximately 1.8 Å with accumulated dose the waste glass samples and a decrease in the corresponding multiple scattering contribution at approximately 3.5 Å. The decrease in the number 'yl' oxygens suggests that concentration of U^{6+} is reduced in the DRG-P2 and DRG-P3 glasses. This effect was also observed in the XANES. In addition, DRG-P1, the lowest dose waste glass sample, exhibits a Fourier transforms feature at approximately 3.5 Å which corresponds to U–U scattering path at 3.62 Å. The occurrence of U–U correlations in a glass that contains only 3.0 weight percent U_3O_8 strongly suggests that clustering of the uranium atoms occurs in the waste glass. Uranium clustering in glass of similar composition has also been observed by Greaves [8].

The Fourier transforms of the Pu L_{III}-edge EXAFS shown in Fig. 1(b), reveal a single Pu–O scattering path. However, curvefitting the EXAFS reveals the Pu–Si and Pu–O contributions. The fitting results in Table 3 show little change in the number of atoms or in sigma, the disorder, of the Pu–O shell with accumulated dose of the waste glass samples. However, the next nearest neighbor

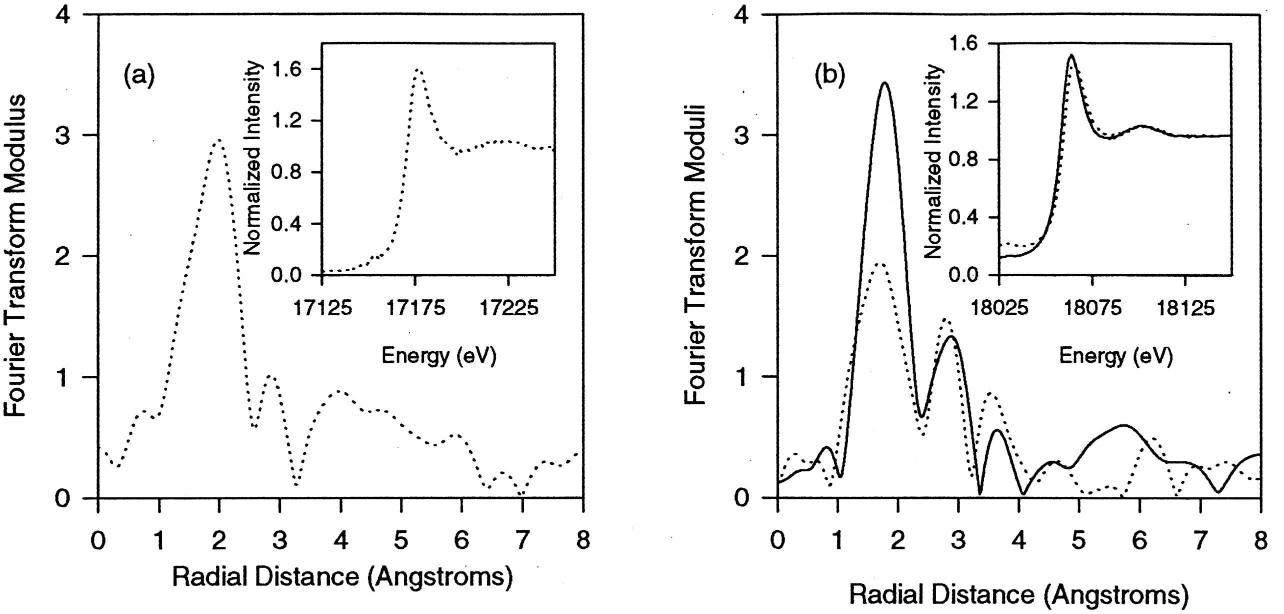

Fig. 2. The Fourier transform of the EXAFS of the Pu-doped zircon at (a) the U L_{III}-edge, and (b) the Pu L_{III}-edge. XANES, are shown in inset. The solid line is the ^{239}Pu-doped zircon and the dotted line is the ^{238}Pu-doped zircon.

shells consisting of Pu–Si, contracts significantly with accumulated α-decay dose.

Zircon. The U and Pu L_{III}-edge XANES spectra of the polycrystalline zircon samples are shown as insets in Fig. 2. All the uranium present in the ^{238}Pu-doped zircon sample formed as the daughter product of ^{238}Pu decay. Because the half-life of ^{239}Pu is much longer than that of ^{238}Pu, only trace amounts of uranium is present in the ^{239}Pu-doped zircon sample. As a result, U XAFS was only collected on the ^{238}Pu-doped zircon sample. The absorption edge energy in the XANES indicates that the oxidation state of U in the ^{238}Pu-doped zircon sample is U^{4+} and the Pu in both zircon samples is Pu^{3+}.

Fits to the U L_{III}-edge EXAFS indicates that the U–O shell consists of two shells separated by approximately 0.2 A, a first shell configuration typical of U^{4+}. However, these bond lengths are too short to be consistent with a model in which the uranium atom forms a coffinite-like structure, the uranium silicate analog of zircon. The short bond lengths and the low number of oxygen atoms in these two shells suggest that uranium is sitting in a highly disordered site. The high degree of disorder around uranium atoms is expected since uranium is the massive α-recoil particle of Pu alpha-decay and create many atomic displacements as it travels ballistically through the lattice.

Analysis of the highly crystalline and fully amorphous zircon Pu L_{III}-edge EXAFS reveal that the local environment around the Pu atoms is similar to that found in the Pu-silicate analog of zircon, $PuSiO_4$. The Pu–O bond distances average 0.20 Å longer than the average Zr–O bond length in pristine zircon. However, the bond lengths of the more distant Zr–Zr/Si and Pu–Zr/Si shells at 3.65 Å are nearly identical. These results suggest that the substitution of Pu^{3+} for Zr^{4+} in the zircon structure creates highly local distortion around the Pu atom that is dissipated at a distance of around 3.5 Å. In addition, the preservation of the Pu environment in the fully amorphous zircon suggests that this configuration is stable at high accumulated alpha-decay doses.

4. Discussion

Analysis of the EXAFS and XANES of the aged waste glass samples indicate that the U and Pu local environments exhibit different degrees of disorder as a result of the accumulated α-decay dose. U atoms show evidence of oxidation state changes in addition to disruption of residual U oligimers whereas the Pu atoms show little effect from self-radiation At high accumulated alpha-decay dose experienced by the zircon samples resulted in amorphization of the zircon structure. U atoms occupy a highly disordered site yet the coordination environment around the Pu cation appears to be preserved.

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