

Probing radiation damage in ceramic wasteforms using X-ray absorption spectroscopy

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ABSTRACT

An understanding of the effect of cumulative radiation damage on the integrity of ceramic wasteforms for plutonium and minor actinide disposition is key to the scientific case for safe disposal. Alpha recoil due to the decay of actinide species leads to the amorphisation of the initially crystalline host matrix, resulting in disruption to the local atomic structure and macroscopic volume swelling. In laboratory studies the effect of radiation damage can be simulated by various methodologies. The incorporation of short-lived actinide isotopes accurately reproduces damage arising from both alpha-particle and the heavy recoil nucleus, but requires access to specialist facilities. Fast ion implantation of inactive model ceramics effectively simulates the heavy recoil nucleus, leading to amorphisation of the host crystal lattice over very short time-scales, and although the resulting materials are easily handled, quantitative analysis of the resulting damaged surface layer is challenging. Our approach to this challenge involves implantation of bulk ceramic samples with Kr⁺ ions, to simulate heavy atom recoil, combined with glancing angle X-ray absorption spectroscopy (GA-XAS) to characterise the damaged surface layer. Here we present experimental GA-XAS data acquired at the Ti K-edges of pyrochlore structured Gd₂Ti₂O₇ demonstrating that this technique can be successfully applied to characterise only the amorphised surface layer. Analysis of the near-edge (XANES) and extended (EXAFS) parts of the absorption spectra have provided evidence for a reduction in the Ti coordination environment during amorphisation.

INTRODUCTION

Assessment of the long-term behaviour of synthetic mineral wasteforms designed for actinide disposition is critical to underpinning the scientific case for their utilisation as disposal matrices. The retention of actinide species in certain mineral systems over geological timescales guides the choice and design of synthetic materials for the disposition of actinide species arising from civilian and military nuclear activities. Whilst natural analogues give confidence in the ability of such systems to retain actinide species over the desired time-scales, the effect of amorphisation, resulting from α -decay of the actinide species, on the crystalline lattice and other key material properties need to be addressed and understood. Several methods exist for simulating radiation damage occurring over disposal timescales. Damage rates can be accelerated by the incorporation of short half life actinide species, generating fully amorphous bulk samples over timescales of several years [1, 2]. *In situ* ion-beam irradiation on thin specimens coupled with inspection of selected

area diffraction patterns allows the determination of the critical ion fluence (ions cm⁻²) required to cause amorphisation under a heavy ion beam flux, at a given temperature [3-5]. In this study irradiation of the surface of Gd₂Ti₂O₇ samples (structure shown in Figure 1) with heavy ions has been combined with *ex-situ* analysis of the specimens by GA-XAS. This technique has previously been employed to study surface oxidation in minerals [6], corrosion layers in glasses [7] and thin films [8].

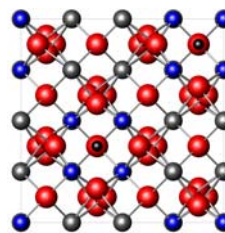


Figure 1 Crystal structure of a pyrochlore structured oxide of A₂B₂O₇ stoichiometry. Grey spheres represent 8-fold coordinated Gd atoms, blue spheres represent 6-fold

coordinated Ti atoms, red spheres represent O atoms and black spheres represent vacancies.

EXPERIMENTAL

The $\text{Gd}_2\text{Ti}_2\text{O}_7$ powder sample was synthesised by conventional solid state sintering using oxide (Gd_2O_3 , TiO_2) precursors. A 50 g powder batch was planetary milled (Retsch PM100) at 250 rpm for 2 hours in a 125 ml stainless steel pot using hardened Cr-steel balls and iso-propanol as the carrier fluid. The powder slurry was then dried for 16 hours at ~ 100 °C. The resulting dry powder cake was sieved (250 μm mesh) and calcined in an alumina crucible, in air, for 10 hours at 1300 °C. The calcine was then sieved again and colloidally milled (Retsch PM100) at 500 rpm in a 125 ml stabilised zirconia pot with 3mm stabilised zirconia media and isopropanol as the carrier fluid. The slurry was dried as above and 20mm diameter pellets approximately 30 mm high were uniaxially pressed at 60 MPa in a hardened stainless steel die. The green pellets were then vacuum sealed in latex gloves and cold isostatically pressed at 200 MPa. The pellets were transferred onto stabilised zirconia setter plates and sintered at 1600 °C for 4 hours. The sintered pellets were sectioned using a low speed diamond saw to afford 1 mm thick cylindrical sections. These sections were then polished to an optical finish (1 μm) and thermally etched at 1450 °C for one hour, to reveal the grain boundaries, and relax out any surface stresses associated with the cutting procedure.

Ion beam irradiation of the monolithic specimens with 2 MeV Kr^+ ions at a fluence of 5×10^{15} ions cm^{-2} was performed at the Ion Beam Centre (IBC) at the University of Surrey, Guildford, UK. The parameters controlling the ion beam irradiation experiment were carefully chosen to maximise the interaction volume for study by XAS. Displacement profiles were calculated using the software package SRIM [9] which predicted that the peak in the damage profile to occur at ~ 800 nm.

Ti K-edge XAS measurements were conducted on beamline X23A2 of the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory (BNL), USA. Transmission measurements were collected using a finely ground specimen of pristine $\text{Gd}_2\text{Ti}_2\text{O}_7$ dispersed in graphite to achieve a thickness of one absorption length. Fluorescence measurements were collected on the pristine and irradiated monoliths with the samples oriented such that the X-ray beam grazed the sample surface at a shallow angle. The samples were mounted on a purpose built stage which could translate in all three directions, to allow accurate positioning of the sample with respect to the beam, and tilt in relation to the plane of the incoming beam to within an accuracy of 0.1°. Glancing angles were selected such as to maintain a path length of at least two absorption lengths within the

800 nm amorphised surface layer, across the range of incident X-ray energies. Since one absorption length corresponds to attenuation of the incident intensity by 66%, at least 95% of detected fluorescence photons thus arise from the surface amorphised layer. A major drawback with fluorescence-mode measurements of concentrated absorbers, as in the current study, is that a significant fraction of fluorescence X-rays may be reabsorbed by the absorber atoms in the sample, causing an attenuation of the fluorescence signal. If uncorrected, such *self-absorption*, leads to a systematic error in determination of nearest neighbour co-ordination numbers. However, XAS data may be satisfactorily corrected for self absorption using well tested algorithms, based on a knowledge of sample density and experiment geometry. All data analysis was performed using ATHENA and ARTEMIS [10].

RESULTS AND DISCUSSION

XANES analysis

The Ti K-edge XANES spectra obtained all exhibit a distinctive pre-edge feature which is attributed to transitions between the Ti 1s and bound Ti 3d / O 2p molecular orbitals. These transitions are forbidden by the dipole selection rule, $\Delta l = \pm 1$, but this is relaxed when the Ti cation is located in a non-centrosymmetric co-ordination environment. Systematic studies have been conducted by Waychunas [11] and Farges [12] which demonstrated that the intensity and position of this pre-edge feature are related to the Ti cation co-ordination and geometry. Figure 2 shows the pre-edge features for the $\text{Gd}_2\text{Ti}_2\text{O}_7$ powder sample measured in transmission and the pristine and irradiated monolithic samples measured by fluorescence in glancing angle geometry. The glancing angle fluorescence data was corrected for self absorption using the Troger algorithm [13]. To ensure the robustness of the self absorption correction the corrected pristine fluorescence data set was compared to the pristine powder sample measured in transmission. This self absorption correction was then applied to the irradiated fluorescence data set. The increase in the pre-edge peak height indicates that the Ti co-ordination environment in the irradiated sample is non-centrosymmetric, in contrast to the pristine material.

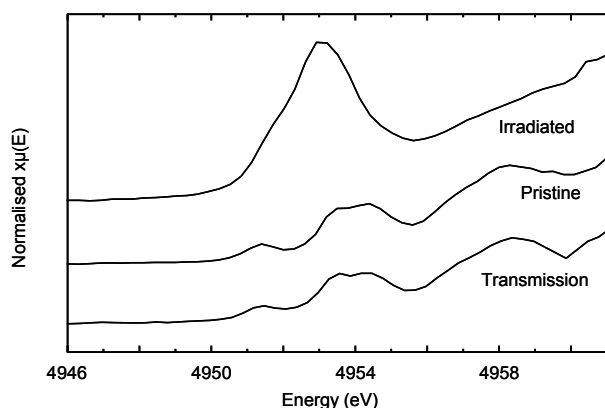


Figure 2 Ti K edge pre-edge XANES feature for powder sample acquired in transmission and pristine and irradiated $Gd_2Ti_2O_7$ samples acquired in glancing angle geometry

Pre-edge peak height and absolute energy positions were extracted according to the methodology proposed by Waychunas [11] and plotted in Figure 3 along with model Ti containing compounds from Farges [12]. Three distinct regions are indicated on the diagram associated with Ti in 6-, 5- and 4-fold co-ordination environments. Overlaid on this are the extracted pre-edge height and absolute energy positions for the pristine and irradiated samples measure in glancing angle geometry and also parameters from from powder samples of two 5-fold coordination standards measured in transmission. The two 5-fold co-ordination standards are Dy_2TiO_5 where the Ti cations are located in trigonal bipyramidal sites and Gd_2TiO_5 where the Ti are located in square pyramidal sites. The pre-edge features for the two different 5-fold geometries both have the same absolute energy position but different heights indicating the different non-centrosymmetric co-ordination environments. As expected the pristine sample shows parameters consistent with 6-fold co-ordinated Ti whilst the parameters for the irradiated sample are more consistent with 5-fold coordinated Ti in mixed trigonal bi-pyramidal and square pyramidal geometry.

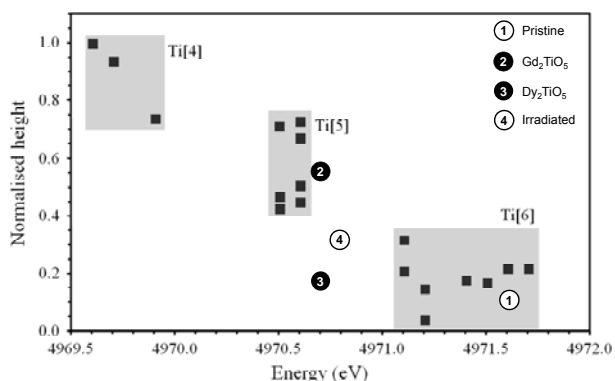


Figure 3 Correlation between Ti co-ordination environment and normalized height and energy position of pre-edge feature in Ti K edge XANES spectra. Solid squares are data from Ti bearing model compounds reported by Farges [12]. Filled and open circles are data from this study.

EXAFS analysis

Analysis of the EXAFS region of the XAS spectrum allows determination of the atoms co-ordinated to the Ti absorber. Figure 4 shows the magnitude of the Fourier transform of the EXAFS data for the pristine pyrochlore sample measured in glancing angle geometry. The intensity in the Fourier transform represents the nearest and next nearest co-ordination shells where the amplitude is related to the number of co-ordinating atoms within a particular shell (N) and the passive electron reduction factor (S_0^2). However, S_0^2 and N are completely correlated and knowledge of one is required to allow determination of the other. Fortunately, for a given experiment at a given edge it can generally be assumed that S_0^2 can be determined uniquely by fitting the measured EXAFS spectrum of a standard of known crystal structure (in this case pristine $Gd_2Ti_2O_7$).

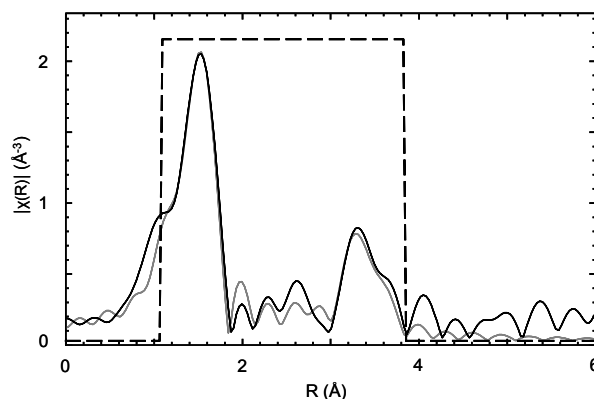


Figure 4 Magnitude of the Fourier transform for the pristine sample measured in glancing angle geometry. Grey line indicates fit to experimental data (black line). Hatched line represents data range over which the model was fitted.

For the pristine sample the co-ordination number of the neighbour atoms was fixed according to the structural model for pyrochlore and the bond distances, thermal parameters and S_0^2 were determined. As can be seen an excellent fit was achieved (Figure 4) and the refined parameters are shown in Table 1.

Table 1 Refined bond lengths, thermal parameters (σ^2) and S_0^2 for pristine sample measured in glancing angle geometry. R-factor indicates quality of fit. N values were fixed according to structural model.

Path	N (fixed)	Model	R(Å) σ^2 (Å ²)
Ti-O	6	1.981	1.981(3)
σ^2 (Ti)	-	-	0.0018(4)
Ti-Gd	6	3.601	3.559(21)
σ^2 (Gd)	-	-	0.0133(40)
Ti-Ti	6	3.601	3.657(6)
σ^2 (Ti)	-	-	0.0009(3)
Ti-O(2)	6	3.758	3.954(22)
σ^2 (O2)	-	-	0.0017(3)
S_0^2		0.55(4)	
R-factor		0.040	

Figure 5 shows the magnitude of the Fourier transform of the EXAFS data for the irradiated

pyrochlore sample measured in glancing angle geometry. The absence of any significant intensity in the Fourier transform beyond the first co-ordination shell indicates a loss of medium to long range crystallographic order and is consistent with Fourier transforms of EXAFS data acquired from disordered system such as glasses. The magnitude of the first shell is reduced in comparison to the pristine sample suggesting a reduction in co-ordination number.

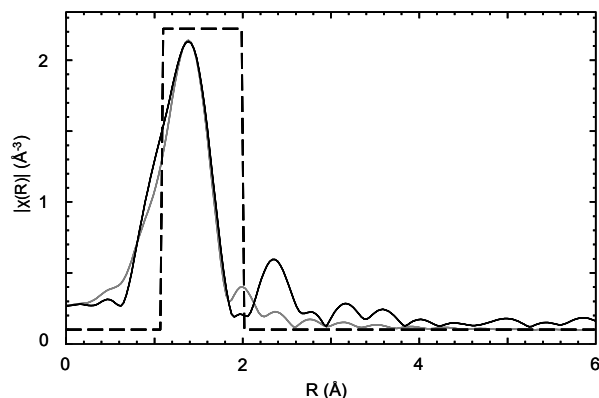


Figure 5 Magnitude of the Fourier transform for the irradiated sample measured in glancing angle geometry. Grey line indicates fit to experimental data (black line). Hatched line represents data range over which the model was fitted.

Data from the irradiated sample was fitted by allowing the contact distance and co-ordination number of the first Ti-O shell to refine, fixing S_0^2 to the value determined previously. The refined parameters are shown in Table 2. The refined co-ordination number was shown to have reduced from 6 to 5.1(3) and there was a concomitant reduction in the first shell Ti-O bond lengths. These findings are in agreement with analysis of the pre-edge XANES feature, as discussed earlier.

Table 2: Refined bond lengths, thermal parameters (σ^2) and N for pristine sample measured in glancing angle geometry. R-factor indicates quality of fit. S_0^2 was fixed.

Path	N	Model	R(Å) σ^2 (Å ²)
Ti-O	5.090(30)	1.981	1.913(7)
σ^2 (Ti)		-	0.0067 (10)
S_0^2		0.55 (fixed)	
R-factor		0.007	

CONCLUSIONS

This work has demonstrated the feasibility of *quantitative* XAS measurements on thin ion beam amorphised surface layers on ceramic specimens. Quantitative XANES and EXAFS analysis has shown, for the first time, that the co-ordination number of Ti is reduced from 6 in pristine $Gd_2Ti_2O_7$ to ~5 in the material amorphised, by heavy ion implantation. A similar analysis has revealed significant changes in the Gd co-ordination environment also. Work is ongoing to apply this methodology to establishing structure-property

relations in radiation amorphised ceramics for actinide immobilization.

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