

FINAL REPORT  
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## **RADIATION EFFECTS IN NUCLEAR WASTE MATERIALS**

Principal Investigator: William J. Weber  
Institution: Pacific Northwest National Laboratory

Contributors: L. R. Corrales, N. J. Ness, R. E. Williford, H. L. Heinisch, S. Thevuthasan,  
J. P. Icenhower, B. P. McGrail, R. Devanathan, R. M. VanGinhoven,  
J. Song, B. Park, W. Jiang  
Institution: Pacific Northwest National Laboratory

Contributor: B. D. Begg  
Institution: Australian Nuclear Science and Technology Organisation

Contributors: R. B. Birtcher, X. Chen  
Institution: Argonne National Laboratory

Contributor: S. D. Conradson  
Institution: Los Alamos National Laboratory

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## **EXECUTIVE SUMMARY**

Radiation effects from the decay of radionuclides may impact the long-term performance and stability of nuclear waste forms and stabilized nuclear materials. In an effort to address these concerns, the objective of this project was the development of fundamental understanding of radiation effects in glasses and ceramics, particularly on solid-state radiation effects and their influence on aqueous dissolution kinetics. This study has employed experimental, theoretical and computer simulation methods to obtain new results and insights into radiation damage processes and to initiate the development of predictive models. Consequently, the research that has been performed under this project has significant implications for the High-Level Waste and Nuclear Materials focus areas within the current DOE/EM mission. In the High-Level Waste (HLW) focus area, the results of this research could lead to improvements in the understanding of radiation-induced degradation mechanisms and their effects on dissolution kinetics, as well as the development of predictive models for waste form performance. In the Nuclear Materials focus area, the results of this research could lead to improvements in the understanding of radiation effects on the chemical and structural properties of materials for the stabilization and long-term storage of plutonium, highly-enriched uranium, and other actinides. Ultimately, this research could result in improved glass and ceramic materials for the stabilization and immobilization of high-level tank waste, plutonium residues and scraps, surplus weapons plutonium, highly-enriched uranium, other actinides, and other radioactive materials.

Extensive progress under this project has resulted in 29 publications. While there have been many advances under this project, the ultimate goal has not yet been reached because of the short duration of the research to date.

## **RESEARCH OBJECTIVES**

The objective of this research was to develop fundamental understanding and predictive models of radiation effects in glasses and ceramics at the atomic, microscopic, and macroscopic levels, as well as an understanding of the effects of these radiation-induced solid-state changes on dissolution kinetics (i.e., radionuclide release). The research performed during the duration of this project has addressed many of the scientific issues identified in the reports of two DOE panels [1,2], particularly those related to radiation effects on the structure of glasses and ceramics. The research approach taken by this project integrated experimental studies and computer simulations to develop comprehensive fundamental understanding and capabilities for predictive modeling of radiation effects and dissolution kinetics in both glasses and ceramics designed for the stabilization and immobilization of high-level tank waste (HLW), plutonium residues and scraps, surplus weapons plutonium, other actinides, and other highly radioactive waste streams. Such fundamental understanding is necessary in the development of predictive models because all experimental irradiation studies on nuclear waste materials are "accelerated tests" that add a great deal of uncertainty to predicted behavior because the damage rates are orders of magnitude higher than the actual damage rates expected in nuclear waste materials. Degradation and dissolution processes will change with damage rate and temperature. Only a fundamental understanding of the kinetics of all the physical and chemical processes induced or affected by radiation will lead to truly predictive models of long-term behavior and performance for nuclear waste materials.

Predictive models of performance of nuclear waste materials must be scientifically based and address both radiation effects on structure (i.e., solid-state effects) and the effects of these solid-state structural changes on dissolution kinetics. The ultimate goal of this project is to provide the scientific understanding and rationale for developing improved glass and ceramic waste forms and to develop scientifically-based predictive models of the near-term (<500 years) and long-term performance of nuclear waste forms and stabilized nuclear materials.

Studies under this project have focused on the effects of ionization and elastic collisions on defect

production, defect interactions, diffusion, solid-state phase transformations, gas accumulation and dissolution kinetics using actinide-containing materials, gamma irradiation, ion-beam irradiation, and electron-beam irradiation to simulate the effects of  $\alpha$ -decay and  $\beta$ -decay on relevant nuclear waste materials. This project has exploited both experimental and computer simulation methods to characterize damage production processes, damage recovery processes, defect migration energies, defect interactions, evolution of microstructure, phase transformations, and dissolution mechanisms, all of which ultimately affect the structural integrity and dissolution kinetics of nuclear waste materials. New atomic-level simulation capabilities, which crosscut both spatial and temporal scales, could lead to more sophisticated predictive capabilities in the future.

## **METHODS AND RESULTS**

### **EXPERIMENTAL STUDIES**

#### **Plutonium-Containing Glasses and Ceramics**

Studies have been performed on polycrystalline zircon samples containing either 10 wt%  $^{238}\text{Pu}$  or 10 wt%  $^{239}\text{Pu}$  and on a suite of compositionally identical plutonium-doped (1 wt%) simulated borosilicate waste glasses prepared with different  $\alpha$ -activities by varying the  $^{239}\text{Pu}/^{238}\text{Pu}$  isotopic ratio. The zircon and glass samples were prepared in 1981 and 1982, respectively. The  $^{238}\text{Pu}$  zircons have achieved an accumulated dose of  $2.8 \times 10^{19}$   $\alpha$ -decays/g, while the  $^{239}\text{Pu}$  zircons have a relatively low accumulated dose of  $1.2 \times 10^{17}$   $\alpha$ -decays/g. The plutonium glasses have accumulated doses of  $9 \times 10^{15}$ ,  $2 \times 10^{17}$ , and  $2 \times 10^{18}$   $\alpha$ -decays/g, which are equivalent to about 20, ten thousand, and one million years of storage, respectively.

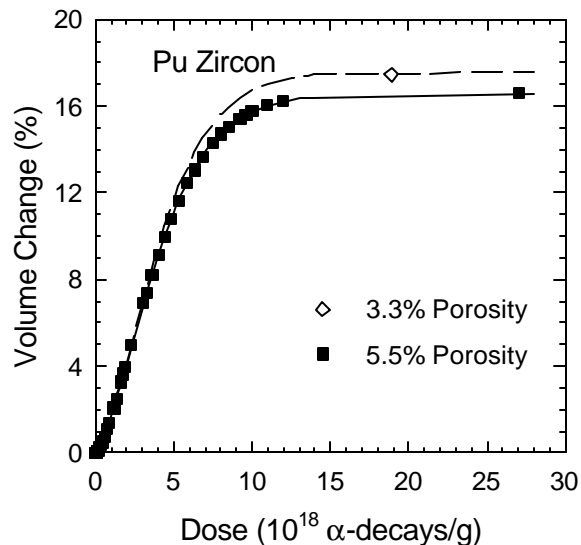
Swelling measurements for the Pu-zircon are summarized in Figure 1. The results show that the swelling is totally saturated at high doses and that the saturation swelling increases with decreasing porosity. When compared with the results for natural zircons (0% porosity), the saturation swelling increases from 16.6% at 5.5% porosity to 18.4% at 0% porosity. In all cases, the swelling can be accurately modeled based on the contributions from crystalline and amorphous components, and a tentative

model of alpha-decay damage in zircon under repository conditions has been developed [3].

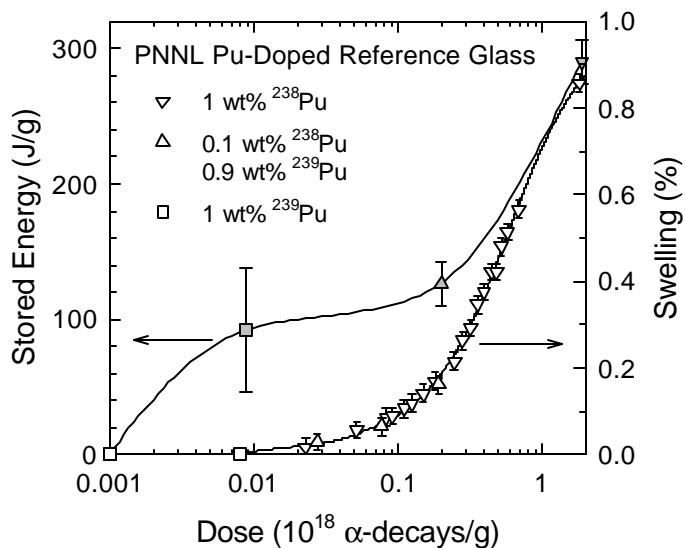
Swelling and stored energy have been measured for the Pu-doped glasses (Figure 2). The results show that the stored energy rapidly increases at very low doses (equivalent to 20 years storage for DOE HLW glasses) and increases to relatively high values at high doses (equivalent to 1 million years storage for DOE HLW glasses). The stored energy could provide a driving force for enhanced dissolution

kinetics by decreasing the energy barrier for dissolution. The swelling does not increase as rapidly with dose, which indicates that the accumulation of defects giving rise to the stored energy precede the rearrangement of the glass network that manifests as volume changes. Electron spin resonance (ESR) measurements on these glasses have also been recently performed by DL Griscom at the Naval Research Laboratory in a collaborative effort with his EMSP project (*Chemical Decomposition of High-Level Nuclear Waste Storage/Disposal Glasses*

*Under Irradiation*). The results indicated no evidence for decomposition to oxidizers (e.g.,  $O_2^-$  or  $O_3^-$ ) or reduced metallic elements; however, the technique is not sensitive to neutral molecular oxygen. Changes in the ESR spectrum of  $Fe^{3+}$  in these glasses have been observed. The results indicate that self-radiation damage from alpha decay causes  $Fe^{3+}$  in some type of cluster to breakup into



**Figure 1.** Swelling in  $^{238}\text{Pu}$ -containing zircon.



**Figure 2.** Stored energy and swelling in PNNL Pu-doped reference waste glasses.

$\text{Fe}^{3+}$  in more isolated sites.

X-ray absorption spectroscopy (XAS) has been performed at six absorption edges for the borosilicate glasses and at three absorption edges for the polycrystalline Pu-zircons [4,5-6]. Analysis of extended x-ray absorption fine structure (EXAFS) spectra for the glasses indicates that the local environment around the cations exhibits different degrees of disorder due to the accumulated  $\alpha$ -decay dose. In general, cations with short cation-oxygen bonds show little effect from self-radiation, whereas cations with long cation-oxygen bonds show a greater degree of disorder with accumulated  $\alpha$ -decay dose. Detailed XAS characterization of the amorphous  $^{238}\text{Pu}$ -substituted zircon is consistent with the loss of both long-range order and edge-sharing relationships between  $\text{SiO}_4$  and  $\text{ZrO}_8$  polyhedra. However, the amorphous state retains a distorted zircon structure and stoichiometry, consisting of  $\text{SiO}_4$  and  $\text{ZrO}_8$  polyhedra rotated relative to each other, over length scales of up to 0.5 nm. The Pu  $L_{\text{III}}$ -edge x-ray absorption near-edge structure (XANES) data for the zircon samples indicate that plutonium is present as  $\text{Pu}^{3+}$  as a result of the reducing conditions (argon atmosphere) under which the plutonium-zircon was synthesized. The plutonium  $L_{\text{III}}$ -edge EXAFS data are consistent with  $\text{Pu}^{3+}$  substitution for  $\text{Zr}^{4+}$  in the zircon lattice. Annealing studies of the Pu-zircons in air indicate that the  $\text{Pu}^{3+}$  is oxidized to  $\text{Pu}^{4+}$  and that direct recrystallization of zircon from the amorphous state is possible at 1200°C, but only if heated rapidly through an intermediate temperature regime (1000°C) where decomposition to oxides is preferred [7,8]. The decomposition of amorphous zircon to constituent oxides is kinetically limited by Zr diffusion, which has a lower energy barrier than the polyhedral rotation required for recrystallization of the zircon structure from the amorphous state.

Diffuse x-ray scattering measurements have been performed on the identical samples on which the XAS studies were conducted. Initial scattering results from the glass samples indicate no change in the silica tetrahedral unit. However, the pair distribution function (PDF) reveals the sharpening of a feature at 0.21 nm with increasing  $\alpha$ -decay dose, which suggests an increase in order for octahedrally coordinated cations. In addition, a feature at 0.27 nm broadens with accumulated  $\alpha$ -decay dose. This distance

corresponds to the O-O distance of the silica tetrahedra, suggesting that O-Si-O bond angle changes may be occurring. The PDF of the zircon diffuse scattering shows strong structure to a distance of 0.5 nm, suggesting that there is significant short-range order in the fully amorphous zircon. Distinct PDF peaks occur at 0.16, 0.21, and 0.37 nm. These distances correspond to the Si-O, Zr-O, and both Zr-Zr and Zr-Si crystallographic distances in crystalline zircon. Consequently, the 0.5 nm unit most likely represents a zirconium center coordinated by first and second-nearest neighbor zirconium atoms and silica tetrahedra.

### **Gamma-Irradiation Studies**

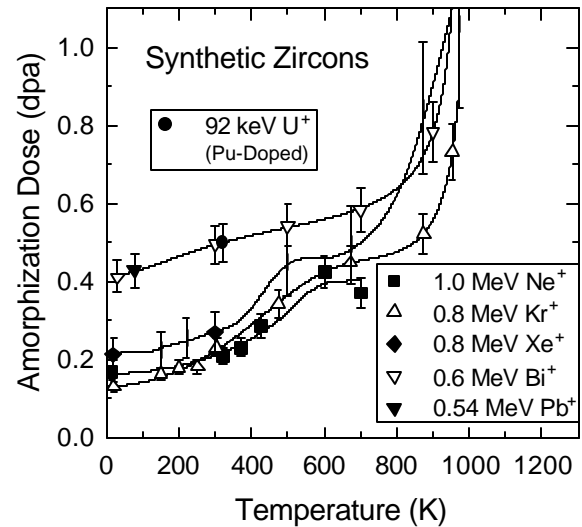
Temperature-controlled capsules were used for irradiation studies within the PNNL ( $^{60}\text{Co}$ ) gamma-irradiation facility. Seven different glasses have been irradiated at four different repository-relevant temperatures (50, 100, 150, and 200°C) over the past three years to doses of 25, 75, and 150 MGy in a study of the effects of fission product decay at relevant temperatures. The highest dose is only equivalent to about 25 years of storage for DWPF glasses, which demonstrates the difficulty in realistically studying the effects of fission product decay. At these dose levels, no significant changes in volume were measured. Only minor changes in the Raman, polarized-Raman, and FTIR spectra are observed. Significant changes, which are believed to be due to electronic defects, are observed in UV-Vis-NIR optical absorption spectra of the Na-borosilicate glass compositions. These radiation-induced variations display systematic dependencies on the irradiation temperature. Some changes in Fe oxidation states have been observed. ESR measurements on some of these glasses have also been performed by DL Griscom at the Naval Research Laboratory in a collaborative effort with his EMSP project (*Chemical Decomposition of High-Level Nuclear Waste Storage/Disposal Glasses Under Irradiation*). The ESR measurements indicate that peroxy radical defects are produced under gamma irradiation at all temperatures in an iron-free simulated waste glass. In an iron-free Na-borosilicate glass, boron-oxygen hole centers are produced under gamma irradiation, and the ESR intensity for these defects decreases with irradiation temperature.



## Electron and Ion Irradiation Studies

### *Amorphization in Zircon*

Single crystals of synthetic zircon ( $\text{ZrSiO}_4$ ) have been irradiated with different ions (from neon to bismuth) over a wide range of temperatures [9]. The results of these studies (Figure 3) show that amorphization in zircon is controlled by a variety of parameters and is a more complex process than previously thought. The critical temperature (975 K) for amorphization appears to be relatively independent of ion mass, and irradiation-induced decomposition is observed above this temperature. The critical amorphization dose in zircon exhibits a two-stage dependence on irradiation temperature and increases with temperature. However, the critical dose for amorphization is significantly higher at lower temperatures (below 500K) for very heavy ions, such as lead and bismuth. This increase in critical dose with the damage energy density has not been observed previously in other materials and is generally inconsistent with direct-impact amorphization as the dominant amorphization process. The data suggest that irradiation with light ions (helium through xenon) may not provide accurate simulation of the dose.



**Figure 3.** Temperature dependence of amorphization in zircon [9].

### *Amorphization in Pyrochlore Structures*

The temperature dependence of the critical dose to completely amorphize  $\text{A}_2\text{Ti}_2\text{O}_7$  pyrochlore structures ( $\text{A}=\text{Y}, \text{Sm}, \text{Gd}, \text{Lu}$ ) under irradiation with 0.6 MeV  $\text{Bi}^+$  ions is shown in Figure 4. There is no significant effect of A-site ion mass on the temperature and dose dependence of amorphization. The amorphization dose exhibits a distinct two-stage dependence on temperature, with a transition temperature between stages at about 500K. Above 950 K, the dose for amorphization rises rapidly as the rate of recovery becomes comparable to the rate of amorphization. At 300 K, the dose to completely amorphize all the samples is on the order of 0.18 dpa, which is similar to that required for  $^{244}\text{Cm}$ -doped

Gd<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub>. Thin sections (~ 1 μm thick) of A<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> pyrochlores were also irradiated, and the structure has been characterized by micro-Raman and micro-XAS techniques. Further work is necessary to refine this approach.

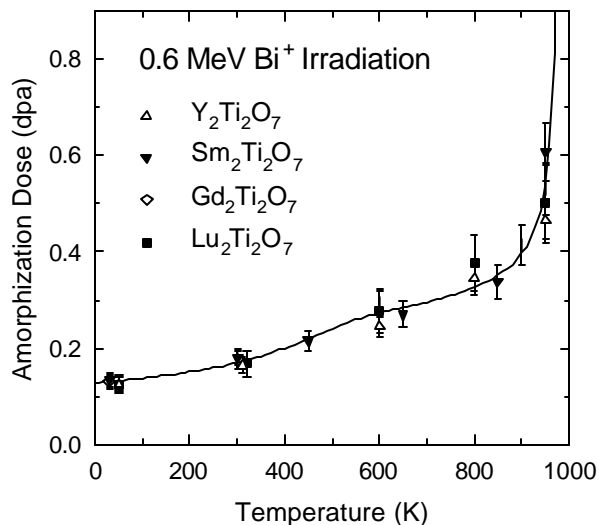
Several bulk A<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> pyrochlores, with near theoretical densities, were also irradiated with 2 MeV Au<sup>+</sup> ions to produce a fully amorphous surface layer to depths of 300 to 400 nm.

Dissolution testing (SPFT method at pH 2) of as-

prepared and irradiated samples was conducted to evaluate the effect of amorphization on dissolution rates and relative reactivities. The dissolution rates for the amorphous state of Gd<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> and Lu<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> were at least an order of magnitude higher than for the crystalline state. The increase in leach rate for Y<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> was less apparent, but the leach rate for the crystalline state of this composition is significantly higher (factor of 10) than for the crystalline states of either Gd<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> or Lu<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub>. Thus, the magnitude of the solid-phase radiation effects on dissolution kinetics is dependent on composition within a given structure. For all three materials, the results suggest incongruent enhanced leaching of the Gd, Lu, and Y relative to Ti. The order of magnitude increase in leach rate for ion-irradiated Gd<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> is consistent with the 20- and 50-fold increase in curium and plutonium release, respectively, measured in amorphous <sup>244</sup>Cm-doped Gd<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> relative to the crystalline state [10]. All these results on pyrochlores are summarized in two publications [11,12].

### *Bubble Formation in Glasses*

Bubble formation in glass is important because it directly affects structural integrity and dissolution kinetics. Gas bubble formation has been observed in simple and simulated waste glasses due to the accumulation of molecular oxygen from radiolytic decomposition or helium from alpha decay. Dose rates



**Figure 4.** Temperature dependence of amorphization in several pyrochlores [11,12].

in laboratory experiments are by necessity 2 to 9 orders of magnitude higher than those expected in actual waste glasses. Bubble formation and the evolution of molecular oxygen are highly dependent on the kinetics of complex and competing processes; thus, observation or lack of observation of bubble formation under laboratory conditions is insufficient data to predict whether such processes will occur in actual waste glasses. A more fundamental understanding of the kinetics of all the competing processes controlling the nucleation and growth of bubbles is needed to predict with any degree of certainty whether bubble formation will occur in actual waste glasses (i.e., to determine whether it is an issue or not).

An electrochemical polishing technique for preparing glass samples was developed that avoids the ion-milling that has been used by previous investigators. Systematic *in situ* studies of irradiation-induced bubble formation in a simple sodium-borosilicate glass have been carried out at 200°C using electrons, as well as helium, krypton, argon, xenon, and oxygen ions [13,14]. This work was performed using the transmission electron microscope (TEM) facilities at Argonne National Laboratory. Oxygen bubbles were not observed to form under oxygen ion implantation at this temperature; however, gas bubbles were observed for all the noble gas implantations. The average bubble size increased with atomic mass of the gas species

## **THEORY, SIMULATIONS AND MODELING**

### **Oxygen Vacancy Migration in Silica**

The pathway and energy for oxygen vacancy migration were calculated in quartz, stishovite, and cristobolite using empirical potentials [15] and density functional theory (DFT) [16] for comparison in the case of quartz. The migration pathway calculations for the oxygen vacancy in quartz, which has a puckered configuration, show similar energetics for the barrier energy using DFT and empirical potentials. The DFT potential provided a more accurate description of the configuration and energies. The lowest energy migration pathway is that in which both the initial and final states are the planar state. The migration pathway calculations in stishovite and cristobolite reveal similarities when compared with the quartz calculations. The existence of backbonding structures, which is a signature of the puckered

configuration, persists in all three crystalline structures.

### **Calculations of the Self-Trapped Exciton in Silica**

Ionization from beta decay during near-term time periods (<500 years) can significantly impact the structure and properties of nuclear waste glasses [1]. Much of this impact comes from the longer-lived electronic excitations, known as self-trapped excitons. The decay of self-trapped excitons can lead to permanent defects. The presence of self-trapped excitons can also lead to significant changes in the migration pathways and energetics of defects and incorporated radionuclides, as well as to modified or enhanced chemical reactivity of the matrix with impurities like water. A computational framework to study these processes did not exist prior to this project. The development of this computational capability has focussed on silica using DFT, *ab initio*, and semi-empirical methods as described below.

#### *Density Functional Theory*

The existence of intrinsic defects in silica can complicate the understanding of how electronic excitations can lead to the formation of point defects. The formation of electron-hole pairs, where the excited electron occupies the lower edge of the conduction band, can lead to a self-trapped exciton state in  $\alpha$ -quartz and silica glass. In such a state, the hole is trapped at an oxygen center and the excited electron at a silicon center. The presence of defects, such as the oxygen vacancy, can change how the electron-hole pair interacts with the lattice depending upon the oxidation state of the vacancy. Moreover, the presence of the electron-hole pair can lead to significant changes in the migration pathways and energetics of the defects.

Work under this project has revealed that there are several self-trapped exciton (STE) states in quartz. There are two oxygen-distorted STE states with a small barrier of about 0.15 eV between them, as well as a silicon-distorted STE that also appears to have a pathway to the other oxygen-distorted STE states. The two oxygen distorted states appear to luminesce at significantly different energies of 4.0 eV and 2.8 eV, whereas the silicon-distorted states appears to be a non-radiative channel for the decay of the STE. The absolute energies cannot be calculated directly with this DFT method; however *ab initio* cluster

calculations have been used to verify these results. New methods are being developed that provide corrections to the absolute energies of the DFT findings. The energies listed in Table 1 are for those determined by DFT without corrections. Only the oxygen-distorted state initially found using DFT is reported.

The excited state configurations and luminescence energies of several oxygen vacancy and interstitial states have been characterized (Table 1). The luminescent energies for these states overlap those of the oxygen- and silicon-distorted STEs, which show two distinct energy bands, as determined by DFT. Confidence in these values have increased since more sophisticated ab initio calculations reveal that the O STE is closer to 4.0 eV and that for the Si STE is virtually a non-radiative channel (i.e., luminescence is not expected). When a Frenkel defect pair is excited, the emission energy is strictly from the oxygen vacancy. In fact, upon exciting the peroxy interstitial, the system undergoes a non-radiative decay back to the ground state with an apparent curve crossing, as the oxygen interstitial system undergoes a configuration relaxation of the ions.

#### *Ab Initio Calculations of Excitons in Silica Clusters*

To verify the results of the DFT calculations for STE in silica, and to more fully characterize the

**Table 1.** Self-Trapped Exciton Absorption ( $E_a$ ), Lattice Relaxation ( $E_{LR}$ ), Luminescent ( $E_e$ ), and Non-Radiative ( $E_{NR}$ ) Energies

	$E_a$	$E_{LR}$	$E_e$	$E_{NR}$
O STE	6.00 <sup>(a)</sup>	-0.47 <sup>(b)</sup>	3.72	2.70
Si STE	6.00 <sup>(a)</sup>	-0.70 <sup>(b)</sup>	0.90	5.80
O neutral vacancy	5.73	2.14	1.09	2.50
O charged vacancy	4.91	0.33	3.12	1.46
O neutral interstitial	4.09	2.80	-	-
O CHARGED INTERSTITIAL	5.77	0.91	4.14	0.72
Defect pair	4.12	2.50	0.95	0.67
(a) This is the delocalized Free Exciton State (FES) of the perfect lattice without distortion.				
(b) The negative sign indicates that these states are higher in energy than the FES.				

newly discovered STE state, ab initio calculations have been performed on silica clusters. Significant improvements have been obtained over the results from previous calculations by increasing the level of theory, the quality of the basis set used in the calculation, and the size of the cluster. The basis set and cluster size dependence for this system has been investigated. In our approach, we have taken a subset of atoms from the DFT periodic calculations in which the STE localization occurs. This cluster can then be accurately calculated by high-level ab initio methods. This technique has allowed us to determine that multiple STE states, as described above, can be connected by low energy pathways [17].

### *Semi-Empirical Simulation Methodology for Excitons Coupled with Phonons*

A novel simulation method that couples the motion of the excited electron and hole with the ionic motion of network atoms has been developed and tested for the crystalline and amorphous states of pure silicon. However, because the application of this method to silica depends on including the proper mechanisms for the formation of the excitons, the work has been put on hold while the silica systems are better characterized using the above ab initio methods. In this method it is important that the electronic states are relaxed faster than the motion of the ions. The time required for relaxing the electronic states into their lowest energy states occurs at a rate comparable to the time steps of the ionic motion, which is about 1.5 to 2 fs. Thus, the method is viable for use in silica systems.

### **Defect Energetics in Crystalline Ceramics**

Activities under this task have been focused on using state-of-the-art computational methodologies to determine fundamental defect energetics in complex crystalline oxides relevant to nuclear waste applications. The most fundamental energy parameters important to radiation effects are the threshold displacement energies,  $E_d$ , for the various cations and anions and the migration energies,  $E_m$ , of radiation-induced defects (e.g., interstitials and vacancies). These energies, which are not easy to determine experimentally, are the fundamental parameters controlling irradiation-induced defect production, defect migration, and the kinetics of microstructure growth and phase transformations. Also important is the relative energy associated with the incorporation of radionuclides, such as plutonium, in the host crystal

structure. Both static energy-minimization methods and molecular dynamics (MD) simulations have been employed to determine these energies.

### *Threshold Displacement Energies by Energy Minimization*

Threshold displacement energies,  $E_d$ , are fundamental parameters controlling the production of radiation-induced defects. These energies are not easily determined experimentally for many ceramic materials; however, advances in computational methodologies and their application to ceramics materials provide a means to determine these energies for a number of ceramic materials of interest. This project pioneered the use of energy-minimization methodology (using the GULP code) to determine  $E_d$  for ceramics of interest (e.g.,  $\text{ZrSiO}_4$ ) and demonstrated that the results of such calculations for oxides ( $\text{MgO}$ ,  $\text{ZnO}$ , and  $\text{Al}_2\text{O}_3$ ) are in excellent agreement (within 14%) with known experimental values [18].

### *Molecular Dynamics Simulations of Displacement Events*

Molecular dynamics (MD) simulations provide a more realistic method to determine  $E_d$  values along specific directions and an atomic-level understanding of displacement processes from near-threshold to much higher (several keV) energies. MD simulations, using a modified version of the DL-POLY code, have been used to obtain threshold displacement energies of atoms along specified directions in  $\text{MgO}$  and  $\text{ZrSiO}_4$ . Ziegler-Biersack-Littmark (ZBL) and Buckingham-type potentials represent the short-range interactions. The long-range Coulombic interactions are evaluated by Ewald sums.

$\text{MgO}$  was chosen as an initial test case because it is one of the simplest oxides and has been extensively studied by both experimental and computational methods. Using a simulation cell consisting of 13,824 atoms at 10 K, the threshold displacement energies were determined along several directions [19]. The minimum displacement energies are 90 eV for Mg and 65 eV for O. The MD simulations reveal the dynamic nature of atomic displacement processes in  $\text{MgO}$  that are probably typical of most oxides.

Compared with  $\text{MgO}$ ,  $\text{ZrSiO}_4$  is a more complex oxide in terms of structural features (open network, directional bonding, multiple cation sites, and distinct bond types), and it is a challenge to develop viable empirical potentials. Using new potentials developed under this project for zircon and a simulation cell

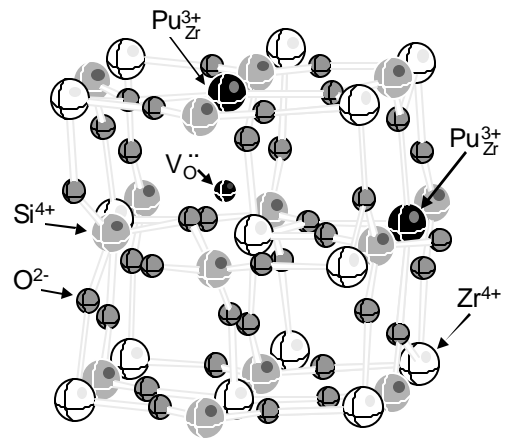
consisting of 12,288 atoms, the threshold displacement energies were determined along a number of directions because of the anisotropic nature of zircon. The minimum displacement energies are 98 eV for zirconium, 48 eV for silicon, and 23 eV for oxygen. However, there is a very strong directional dependence for the displacement energies, and subthreshold displacement energies on one sublattice can lead to displaced atoms on another sublattice [20].

### *Vacancy Migration in $\text{ZrSiO}_4$*

Two sets of interatomic potentials were selected to study the migration of zirconium, silicon, and oxygen vacancies in zircon: one with O-Si-O three-body terms for the  $\text{SiO}_4$ , and one without. Results [21] show that both zirconium and oxygen vacancies can migrate on fully connected three-dimensional networks within the zircon lattice. The lowest-energy pathway for the zirconium vacancy is between nearest-neighbor zirconium sites, with an activation energy of 1.2 or 1.4 eV, depending on the potentials used. The lowest-energy pathway for the oxygen vacancy is along the unshared  $\text{ZrO}_8$  dodecahedra edges, with an activation energy of 1.2 or 1.0 eV, depending on the potentials. Results for silicon were inconclusive, but are consistent with the structural stability of the  $\text{SiO}_4$  tetrahedra.

### *Stable Configurations for Plutonium Substitution in $\text{ZrSiO}_4$*

As noted above, XAS experiments on Pu-substituted zircons under this project have confirmed that the Pu in the originally prepared and radiation-damaged samples occurs as  $\text{Pu}^{3+}$  because of the original preparation under reducing conditions. More recent XAS studies under this project have revealed that by annealing the samples in air the  $\text{Pu}^{3+}$  state is oxidized to  $\text{Pu}^{4+}$  [7,8]. Energy minimization methods have been used to determine the energetics of  $\text{Pu}^{3+}$  and  $\text{Pu}^{4+}$  incorporation in zircon (as interstitials or as substitutions on zirconium sites) to identify the most stable defect configuration for each



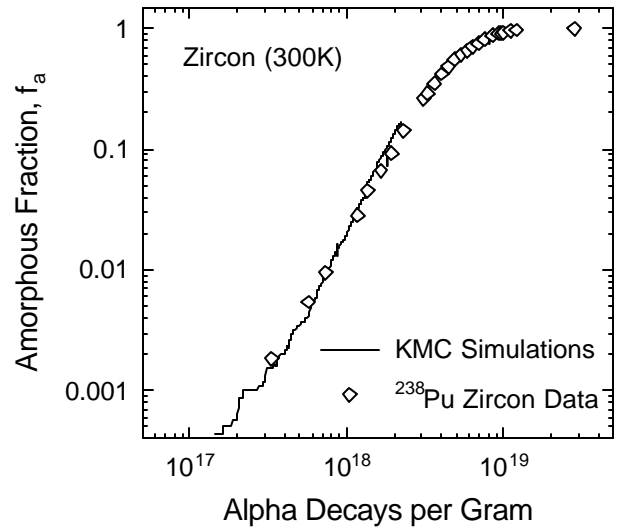
**Figure 5.** The  $2\text{Pu}^{3+}_{\text{Zr}} + \text{V}_\text{O}^{\bullet\bullet}$  cluster in zircon [22].



oxidation state and to assist in the interpretation of XAS data [22]. The lowest-energy configuration for  $\text{Pu}^{3+}$  incorporation is as a defect cluster consisting of two closely associated  $\text{Pu}^{3+}$  ions on zirconium sites and an oxygen vacancy for charge compensation, as shown in Figure 5. The resulting polarized defect cluster has a lower energy than isolated  $\text{Pu}^{3+}$  on zirconium sites and charge-compensating oxygen vacancies. The lowest-energy configuration for  $\text{Pu}^{4+}$  is as a substitution on a zirconium site, which is consistent with the recent XAS data. Mean-field calculations of the unit-cell volumes using these lowest energy configurations for 8%  $\text{Pu}^{3+}$  or  $\text{Pu}^{4+}$  substitution for zirconium (as in the actual samples) are in good agreement with recent x-ray diffraction data on these samples [8].

### Evolution of Damage on Longer Length and Time Scales

Kinetic Monte Carlo (KMC) simulations can be used to study the evolution of radiation damage at the atomic scale over times and distances well beyond those possible with MD simulations. In principle, KMC simulations can be used to study self-radiation effects, such as amorphization, in nuclear waste materials over laboratory to geologic time scales. Our current approach uses cascades generated by the binary simulation code MARLOWE as the defect production input. Eventually, results that are more realistic will be available from the MD simulations. Single vacancies and interstitials representing the cascade-generated defects are inserted into the simulation. The kinetics of migration and interaction for individual defects are followed within the crystal lattice, but interactions of individual atoms are not dealt with explicitly. Defects are assumed to migrate only on their own sublattice. When a vacancy and interstitial defect become nearest neighbors (on their own sublattice), they are recombined. Same-type



**Figure 6.** Comparison of KMC simulations with experimental results [23].

defects associated with nearest neighboring sites are assumed to form an immobile cluster. Collision cascades are inserted into the simulation volume randomly in space and time at a predetermined average rate. After each cascade occurs, the cascade region is searched for amorphization based on defect density, and regions with a defect density above a critical value are designated as “amorphous.”

Defect accumulation and amorphization in zircon doped with plutonium have been simulated for a cell volume, 72 lattice parameters on a side, using 1000 MARLOWE cascades for 94 keV  $^{234}\text{U}$  recoils. This represents a cumulative dose of about  $2.2 \times 10^{18}$  alpha decays/g (or 0.093 dpa). The simulation results for the amorphous fraction as a function of dose are in excellent agreement with the experimental results of Weber [23], as shown in Figure 6.

## **RELEVANCE, IMPACT, AND TECHNOLOGY TRANSFER**

Radiation effects from the decay of radionuclides may impact the long-term performance and stability of nuclear waste forms and stabilized nuclear materials. Thus, the research performed under this project has significant implications for the High-Level Waste and Nuclear Materials focus areas within the current DOE/EM mission. In the High-Level Waste (HLW) focus area, the results of this research could lead to improvements in the understanding of radiation-induced degradation mechanisms and their effects on dissolution kinetics, as well as development of predictive models for waste form performance. In the Nuclear Materials focus area, the results of this research could lead to improvements in the understanding of radiation effects on the chemical and structural properties of materials for the stabilization and long-term storage of plutonium, highly-enriched uranium, and other actinides. Consequently, this research could result in improved glass and ceramic materials for the stabilization and immobilization of high-level tank waste, plutonium residues and scraps, surplus weapons plutonium, highly-enriched uranium, other actinides, and other radioactive materials.

## **PROJECT PRODUCTIVITY**

The project did not accomplish all of its goals because of the initial 25 percent reduction in budget and because of the short (3-year) duration of actual funding. The overall objective was a much longer-

term goal related to eventual performance assessment criteria that could not be achieved in just a 3-year effort. Nonetheless, most of the goals for the initial 3-year phase of the originally proposed work were accomplished and on schedule.

## **PERSONNEL SUPPORTED**

Dr. William J. Weber (Principal Investigator), Pacific Northwest National Laboratory (PNNL)

### **Other PNNL Staff**

L. R. Corrales, N. J. Ness, R. E. Williford, H. L. Heinisch, S. Thevuthasan, J. P. Icenhower,  
B. P. McGrail, G. D. Maupin, M. J. Schweiger

### **Postdoctoral Fellows**

R. Devanathan (PNNL), J. Song (PNNL), B. Park (PNNL), W. Jiang (PNNL), X. Chen (ANL)

### **Graduate Student**

R. M. VanGinhoven (University of Washington) - Because funding for this project was terminated on September 30, 1999, Ms. VanGinhoven was forced to seek funding elsewhere to complete her Ph.D. The experience has left her with an unfavorable impression of DOE/EM.

### **Visiting Scientist**

B. D. Begg (Australian Nuclear Science and Technology Organisation)

### **Staff at other DOE Laboratories**

R. B. Birtcher (Argonne National Laboratory)

S. D. Conradson and M. Nastasi (Los Alamos National Laboratory)

## **PUBLICATIONS**

### **Books**

I. Muller, W. J. Weber, E. R. Vance, G. G. Wicks and D. G. Karraker, **Chapter 12: Plutonium in Crystalline Ceramics and Glasses**, in *Advances in Plutonium Chemistry (1967 to 1999)*, edited by D. C. Hoffman (American Nuclear Society, LaGrange Park, Illinois, 2000) submitted.

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## INTERACTIONS

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2. W. J. Weber, N. J. Hess, S. D. Conradson, and J. D. Vienna, "Self-Radiation Effects in Glass and Ceramic Waste Forms for the Stabilization and Disposition of Plutonium," Topical Conference on *Plutonium Futures - The Science*, Santa Fe, NM, August 25-27, 1997.
3. L. R. Corrales and J. Song, "Molecular Dynamics Simulations of Excitons in Glasses," CEA/VALHRO Summer School, Mejjannes le Clap, France, September, 1997.
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6. N. J. Hess, W. J. Weber, and S. D. Conradson, "X-ray Absorption Fine Structure of Aged, Pu-Doped Glass and Ceramic Waste Forms," MRS Symposium on *Scientific Basis for Nuclear Waste Management XXI*, Davos, Switzerland, September 28 - October 3, 1997.
7. L. R. Corrales "Lattice Theories and Molecular Dynamics Simulations of Glasses," Department of Chemistry, University of Maryland, College Park, MD, October, 1997.
8. L. R. Corrales, "Molecular Dynamics Simulations of Defects and Excitons in Glasses", American Ceramics Society, Glass and Optical Materials Division Meeting, Williamsburg, VA, October 1997.
9. W. J. Weber, "Radiation Effects in Glass and Ceramic Waste Forms" (**Invited Seminar**), Massachusetts Institute of Technology, Cambridge, MA, December 1, 1997.
10. R. Devanathan, W. J. Weber, and L. A. Boatner, "Response of Zircon to Electron and Ne<sup>+</sup> Irradiation," Materials Research Society Annual Meeting, Boston, MA, December 1-5, 1997.
11. W. J. Weber, "Radiation Effects in Glass Waste Forms" (**Invited Seminar**), Argonne National Laboratory, Argonne, IL, December 11, 1997.
12. W. J. Weber, "Radiation Effects in Crystalline Waste Form Phases" (**Invited Seminar**), Idaho National Engineering and Environmental Laboratory, Idaho Falls, ID, January 8, 1998.
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15. W. J. Weber, "Radiation Effects from Alpha Decay in Nuclear Waste Ceramics" (**Invited Plenary Lecture**), American Nuclear Society Northern Student Conference, Ann Arbor, MI, April 3-4, 1998.

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21. W. J. Weber, R. Devanathan, A. Meldrum, L. A. Boatner, R. C. Ewing, and L. M. Wang, "The Effect of Temperature and Recoil Spectra on Amorphization in Zircon," Materials Research Society Annual Meeting, Boston, MA, November 30 - December 4, 1998.
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32. L. R. Corrales, J. Song, R. M. VanGinhoven and H. Jónsson, "The Formation and Migration Energetics of Radical Defects in Silica Polymorphs" (**Invited Paper**), The 101<sup>st</sup> Meeting of The American Ceramic Society, Indianapolis, IN, April 25-28, 1999.
33. B. D. Begg, W. J. Weber, R. Devanathan, J. P. Icenhower, S. Thevuthasan, and B. P. McGrail, "Heavy-Ion Irradiation Effects in Pyrochlores," The 101<sup>st</sup> Meeting of The American Ceramic Society, Indianapolis, IN, April 25-28, 1999.
34. R. E. Williford and W. J. Weber, "Defect Formation and Migration Energetics in Disordered  $\text{Gd}_2\text{Ti}_2\text{O}_7$ ," The 101<sup>st</sup> Meeting of The American Ceramic Society, Indianapolis, IN, April 25-28, 1999.
35. B. Park, L. R. Corrales, and W. J. Weber, "Computer Simulation of Collision Cascades in Zircon," The 1999 Fall Meeting of the Materials Research Society, Boston, MA, November 29 - December, 1999.
36. W. J. Weber, "Radiation Effects in Nuclear Waste Materials" (**Invited Presentation**), *EMSP National Workshop on Science Applications*, Atlanta GA, April 25-27, 2000.

## TRANSITIONS

Currently, all transitions have been in the form of open literature publications and presentations.

Since the product at this stage is new underpinning science for predictive models that can be ultimately used for performance assessment, no additional transitions to technology or applications have been made.

## PATENTS

No patents were filed or obtained under this project.

## FUTURE WORK

Eight manuscripts in various steps of preparation need to be completed or the results of this work will never be published. Research over another 3-year period is needed to continue the development of fundamental understanding and predictive models for solid-state radiation effects; however, there needs to be an increased effort on understanding the effects of these solid-state changes on dissolution kinetics, which is the path by which radionuclides are released to the environment. The detailed characterization, conducted under this project, of the radiation-induced changes in structure, coordination, valence states, density and stored energy in the Pu-doped glasses and Pu-substituted zircons provides an invaluable opportunity to determine the ultimate impact of these changes on the stability of glasses and ceramics



when contacted by water. Understanding the aqueous dissolution kinetics of these materials is of obvious importance in predicting their long-term performance in a geologic repository. One of the goals under any renewed funding would be to integrate the new understanding gained on fundamental mechanisms (from the studies on actinide-containing materials, ion-beam-irradiated materials, dissolution kinetics, and computer simulations) into improved predictive models of long-term behavior and performance.

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