

Project ID: **54672**

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Project Title: **Radiation Effects in Nuclear Waste Materials**

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Radiation Effects in Nuclear Waste Materials

(First Year of Funding: 1996)

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Research Objective

The objective of this multidisciplinary, multi-institutional research effort is to develop a fundamental understanding of radiation effects in glasses and ceramics at the atomic, microscopic, and macroscopic levels. Current research addresses many of the scientific issues identified in the reports of two recent DOE panels (Weber et al. 1997, 1998). The goal of this effort is to provide the underpinning science and models necessary to assess the performance of glasses and ceramics designed for the immobilization and disposal of high-level tank waste, plutonium residues, excess weapons-grade plutonium, and other highly radioactive waste streams. Studies are focused on the effects of ionization and elastic collisions on defect production, defect interactions, diffusion, solid-state phase transformations, and gas accumulation using actinide-containing materials, gamma irradiation, ion-beam irradiation, and electron-beam irradiation to simulate the effects of α -decay and β -decay on nuclear waste materials. This program exploits a variety of structural, optical, and spectroscopic probes to characterize the nature and behavior of defects, defect aggregates, and phase transformations. Computer simulation techniques are also used to determine defect production processes, defect energies, and defect/gas diffusion and interactions. A number of irradiation facilities and capabilities are used, including user facilities at other national laboratories, to study the effects of irradiation under different conditions.

Problem Statement

A significant challenge facing the environmental management and restoration activities at DOE facilities is the stabilization and immobilization of high-level tank waste, high-level sludge in fuel storage basins, and plutonium residues/scrap. In addition, the immobilization and disposal of surplus weapons-grade plutonium is becoming a growing technological and political issue that is historically and politically tied to environmental management and restoration activities. These high-level wastes will be converted to glass or glass-ceramic waste forms for permanent disposal in a geologic repository. A key challenge is to develop predictive strategies and models, based on sound scientific understanding, to fully assess long-term performance. Self-radiation effects from α -decay and β -decay can significantly impact long-term performance. Waste forms for the disposal of plutonium residues/scrap, surplus weapons-grade plutonium, and other high-actinide waste streams may differ significantly in composition from the waste forms for high-level tank wastes and will produce significantly higher radiation doses and helium. The current baseline data and scientific understanding of radiation effects in glasses, glass-ceramics, and crystalline phases are critically lacking. Without a fundamental understanding of radiation effects at the molecular, microscopic, and macroscopic levels, meaningful predictions of performance are not possible. This lack of understanding of the radiation damage processes that occur in nuclear waste materials makes it impossible to extrapolate the limited existing data bases to larger doses, lower dose rates, longer time periods, different temperature regimes, and different glass compositions or ceramic structures.

Research Progress

There has been extensive progress under this project, and work to date has resulted in a number of publications, which are listed at the end of this report. Highlights of the research over the past year are presented below.

Theory, Simulations, and Modeling

Oxygen Vacancy Migration in Silica

The migration pathway and energy of an oxygen vacancy were calculated in quartz, stishovite, and cristobolite using empirical potentials. For comparison, the minimum energy pathway in quartz was calculated using a density functional theory (DFT) interatomic potential. The differences between the two potentials' types show that although the energies of both approaches are similar, the pathways and hence the mechanisms of diffusion are different.

The migration pathway calculations for the oxygen vacancy in quartz show similar energetics for the barrier energy using DFT and the BKS (Van Beest, Kramer, and Van Santen) (Van Beest et al. 1990) potentials. However, the underlying mechanism for diffusion is clearly different. The BKS potential has as its initial and final states a puckered structure for the vacancy defect. Although DFT also predicts the puckered configuration as the lowest energy state, it also shows that there is a barrier of 0.6 eV towards a metastable planar configuration. The lowest lying migration pathway is that in which both the initial and final states are the planar state. Thus, distinct differences in the pathway, the degree of network relaxation, and path length are seen between the two calculation methods.

The migration pathway calculations in stishovite and cristobolite reveal similarities (and also some differences) when compared with the quartz calculations. These were calculated using only the BKS potential. The existence of backbonding structures, which is a signature of the puckered configuration, persists in all three crystalline structures. It would thus be valuable to carry out more detailed DFT calculations of the vacancy defect in these crystal structures to determine the stable and metastable structures, as in quartz.

Calculations of the Self-Trapped Exciton in Silica

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 α -quartz where the lattice (or bond) is distorted. In such a state, the hole is trapped at an oxygen center and the excited electron at a silicon center. The presence of a point defect, such as the oxygen vacancy, can change how the electron-hole pair interacts with the lattice depending upon the oxidation states of the vacancy. Moreover, the presence of the electron-hole pair can lead to significant changes in the migration pathways and energetics of the point defect.

Recent work under this project has revealed that there are several self-trapped exciton (STE) states in quartz, one of which is the same as that first determined by ab initio calculations of Fisher et al. (1990). In addition to the lowest-energy-oxygen-distorted STE, there is a silicon-distorted STE at an energy of 0.23 eV higher. These two states appear to luminesce at significantly different energies; however, the absolute energies cannot be calculated with this DFT method. Instead, new methods are being developed to determine the absolute energies and carry out ab initio calculations to verify these DFT findings.

The excited state configurations and luminescence energies of several oxygen vacancy and interstitial states have also been characterized, as given in [Table 1](#). The luminescent energies for these states overlap those of the oxygen and silicon-distorted STEs, which also show two distinct energy bands. When a Frenkel defect pair is excited, the emission energy is strictly from the oxygen vacancy. In fact,

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 ^(a)	-0.47 ^(b)	3.72	2.70
Si STE	6.00 ^(a)	-0.70 ^(b)	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.

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. This work will be submitted for publication.

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 newly discovered STE state, ab initio calculations are being performed on silica clusters. Significant improvements have been obtained over the results from previous calculations of Fisher et al. (1990) by increasing the level of theory, the quality of basis set used in the calculation, and the size of the cluster. The basis set and cluster size dependence for this system is being investigated. The minimum cluster size to adequately describe the new STE state is $\text{Si}_5\text{O}_{16}\text{H}_{12}$. The minimum level of theory required is second-order Moller-Plesset Perturbation (MP2) with a 6-31G* basis set. Calculations of the required size will take some additional time to complete.

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 ab initio methods. In the work on silicon, which is being submitted for publication, coupling of the electronic states with the ionic motion has been successfully implemented.

The time scales for relaxing the electronic states into their lowest energy states happens 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 but requires further development.

Defect Energetics in Crystalline Ceramics

Activities under this task are 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, particularly for multication ceramics, are the fundamental parameters controlling irradiation-induced defect production, defect migration, and the kinetics of microstructure growth and phase transformations. Also important is the energy change associated with the incorporation of radionuclides, such as plutonium, in the host crystal structure. Both static energy-minimization methods and molecular dynamics (MD) simulations are being employed under this project to determine these energies.

Threshold Displacement Energies in MgO and ZrSiO₄. Molecular dynamics simulations are used to obtain threshold displacement energies of atoms along specified directions in MgO and ZrSiO₄. The MD code, DL_POLY (a general purpose, parallel molecular simulation package developed by Daresbury Laboratory, UK) has been modified to implement irradiation phenomena. Ziegler-Biersack-Littmark (ZBL) and Buckingham-type potentials represent the short-range interactions. The long-range Coulombic interactions are evaluated by an Ewald method.

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. The simulation cell consists of 13,824 atoms with periodic boundary conditions in all three directions. The simulations are carried out at 10K. An atom in the center of the cell is given kinetic energy along a specific direction, and the positions and kinetic energies of all neighboring atoms are monitored as a function of time. The threshold displacement energy is the kinetic energy at which a permanent displacement (interstitial or replacement) is produced. Several directions have been investigated, and the minimum displacement energies in MgO are 90 eV for Mg and 65 eV for oxygen. The MD simulations have revealed the dynamic nature of atomic displacement processes in MgO, and the results of this study will be submitted for publication.

Compared with MgO, ZrSiO₄ is a rather 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. A new potential parameter set for ZrSiO₄ based on the rigid ion model has been developed under this project. The total number of atoms used in the displacement simulations for ZrSiO₄ is 12,288, and the computational procedures are the same as for MgO. A larger number of directions is needed to account for the anisotropic nature of ZrSiO₄. A total of 15 different directions have been examined to date. 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.

Vacancy Migration in ZrSiO₄. Based on this project's previous experience in computing displacement energies in zircon (Williford et al. 1998), 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 SiO₄, and one without. Results 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 potential used. The lowest-energy pathway for the oxygen vacancy is along the unshared ZrO₈ dodecahedra edges, with an activation energy of 1.2 or 1.0 eV, depending on potential. The experimental activation energy (Cherniak et al. 1997) for self-diffusion on the zirconium sublattice (7.5 to 8.7 eV) is consistent with the sum of the zirconium vacancy formation (6.2 eV) and migration (1.2 to 1.4 eV) energies. Similarly, the activation energy (Watson and Cherniak 1997) for self-diffusion on the oxygen sublattice (4.6 eV) is consistent with the sum of the oxygen vacancy formation (3.3 eV) and migration (1.0 to 1.2 eV) energies. Results for silicon were inconclusive, but are consistent with the structural stability of the SiO₄ tetrahedra.

Stable Defect Configuration for Plutonium Substitution in ZrSiO₄. X-ray absorption spectroscopy (XAS) experiments (Hess et al. 1998) on plutonium-containing zircons studied under this project have confirmed that the plutonium in the originally prepared and radiation-damaged samples occurs as Pu³⁺ because of the original preparation under reducing conditions. More recent XAS studies, as discussed below, have revealed that by annealing the samples in air the Pu³⁺ state is oxidized to Pu⁴⁺. Energy minimization methods have been used to determine the energetics of Pu³⁺ and Pu⁴⁺ incorporation in zircon (as interstitials or as substitutions on zirconium sites) to identify the most stable defect configuration for each oxidation state and to assist in the interpretation of XAS data. The lowest-energy configuration for Pu⁴⁺ was as a substitution on a zirconium site, which is consistent with the recent XAS data. The lowest-energy configuration for Pu³⁺ incorporation was as a defect cluster consisting of two closely associated Pu³⁺ ions on zirconium sites and an oxygen vacancy for charge compensation. The resulting polarized defect cluster has a lower energy than isolated Pu³⁺ on zirconium sites and charge-compensating oxygen vacancies. In the lowest-energy cluster (Figure 1), the two Pu³⁺ ions are arranged in a right angle configuration with the oxygen vacancy at the center. Incorporation of Pu³⁺ or Pu⁴⁺ as interstitials is energetically prohibited. Mean-field calculations of the unit-cell volumes using these lowest energy configurations for 8% Pu³⁺ or Pu⁴⁺ substitution for zirconium (as in actual samples) are in good agreement with recent x-ray diffraction data on these samples.

Evolution of Damage from Alpha-Recoil Cascades in ZrSiO₄

Kinetic Monte Carlo (KMC) simulations are being 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. Single vacancies and interstitials representing the cascade-generated defects are inserted into the simulation. The kinetics of individual defects hopping on the crystal lattice are followed, but interactions of individual atoms are not dealt with explicitly. Defects are assumed to migrate only on their own sublattices. When a vacancy and interstitial defect become nearest neighbors (on their own sublattice), they are recombined. Same-type

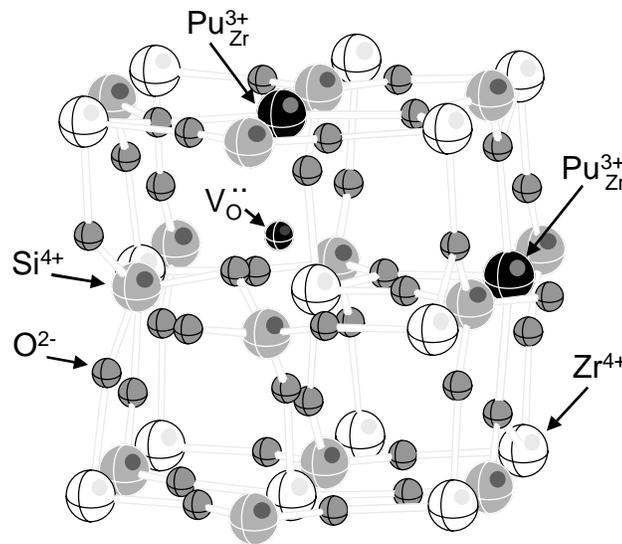


Figure 1. The Defect Cluster $2\text{Pu}_{\text{Zr}}^{3+} + \text{V}_{\text{O}}^{\bullet\bullet}$ in Zircon, Viewed Along the [001] Direction

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 assumed “amorphous.”

Defect accumulation and amorphization in zircon doped with plutonium have been simulated in a rectangular simulation volume, 72 lattice parameters on a side, using 1000 MARLOWE cascades for 94 keV ^{234}U recoils. This represents a cumulative dose of about 2.2×10^{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 experimental results (Weber et al. 1994), as shown in [Figure 2](#). The effects of recoil spectra, dose, and dose rate are being explored to examine the differences between amorphization of plutonium-doped, natural and ion-irradiated zircon using this model.

Experimental Studies

Plutonium-Containing Glasses and Ceramics

Studies have continued on polycrystalline zircon samples containing either 10 wt% ^{238}Pu or 10 wt% ^{239}Pu and a suite of compositionally identical plutonium-doped (1 wt%) waste glasses prepared with different α -activities by varying the $^{239}\text{Pu}/^{238}\text{Pu}$ isotopic ratio. The zircon and glass samples were prepared 17 and 16 years ago, respectively. The ^{238}Pu zircons (5.6×10^{10} Bq/g) have achieved an accumulated dose of 2.8×10^{19} α -decays/g, while the ^{239}Pu zircons (2.5×10^8 Bq/g) have a relatively low accumulated dose of 1.2×10^{17} α -decays/g. The plutonium glasses, with α -activities ranging from 1.9×10^7 to 4.2×10^9 Bq/g, have accumulated doses between 8.8×10^{15} to 1.9×10^{18} α -decays/g.

Swelling measurements for the plutonium-zircon are summarized in [Figure 3](#). 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 (Weber 1993), 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.

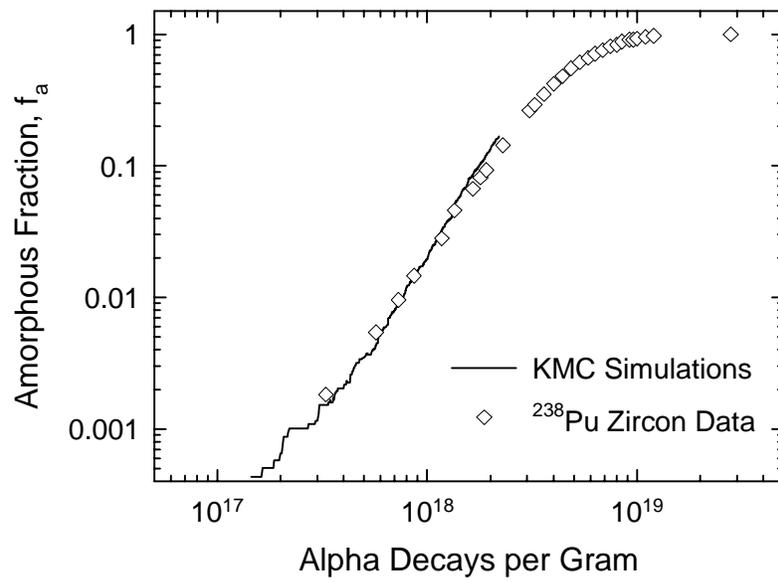


Figure 2. Comparison of KMC Simulations with Experimental Results of Weber et al. (1994)

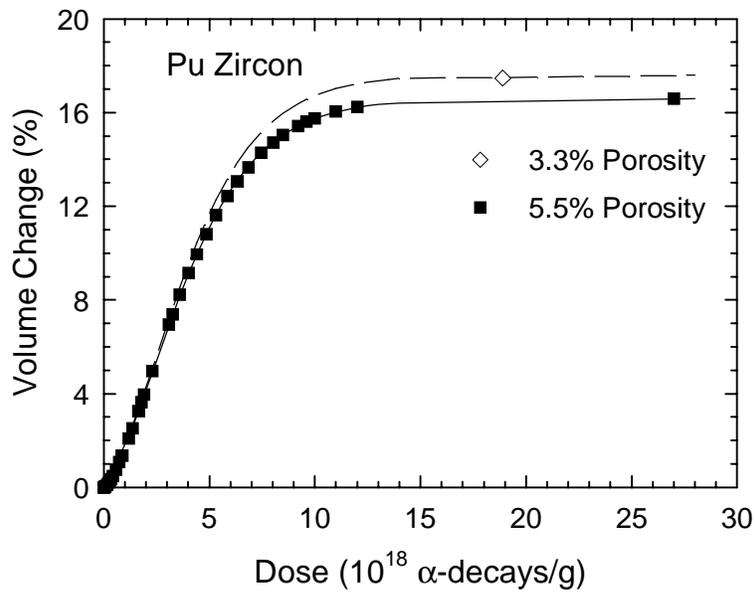


Figure 3. Swelling in Plutonium-Doped Zircon

The multicomponent composition of the plutonium-containing glasses and zircons permitted XAS investigations at six absorption edges for the borosilicate glasses and at three absorption edges for the polycrystalline plutonium-zircons. For all materials, analysis of extended x-ray absorption fine structure (EXAFS) spectra indicates that the local environment around the cations exhibits different degrees of disorder as a result of the accumulated α -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 α -decay dose. The plutonium L_{III} -edge x-ray absorption near-edge structure (XANES) data for the zircon samples indicate that plutonium is present as Pu^{3+} as a result of the reducing conditions (argon atmosphere) under which the plutonium-zircon was synthesized. The plutonium L_{III} -edge EXAFS data are consistent with Pu^{3+} substitution of Zr^{4+} in the zircon lattice, as also predicted by the computer simulation results discussed above.

Diffuse x-ray scattering measurements have been performed on the identical samples on which the earlier XAS studies were conducted. Initial scattering results of 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 α -decay dose, which suggests an increase in order for octahedrally coordinated cations. In addition, a feature at 0.27 nm broadens with accumulated α -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. As a result, the 0.5 nm unit most likely represents a zirconium center coordinated by first and second-nearest neighbor zirconium atoms and silica tetrahedra. These recent results provide additional insight into the phenomenon of self-radiation damage in glass and ceramic waste forms.

An initial series of annealing studies under oxidizing conditions has been conducted on the zircon samples to determine the distribution of Pu^{4+} in the amorphous and crystalline structure. The amorphous ^{238}Pu -doped zircon was annealed in air at 1000 and 1200°C for 12 hours. The crystalline ^{239}Pu -doped

zircon was annealed in air at 1200°C for 12 hours. XANES, EXAFS, and PDF analysis were used to determine the oxidation state, local structure, and radial distribution of the zirconium, plutonium, and uranium cations. Analysis of the plutonium L_{III}-edge XANES indicates oxidation of Pu³⁺ to Pu⁴⁺ in all the annealed zircon samples. Analysis of zirconium K-edge and plutonium L_{III}-edge EXAFS of the ²³⁸Pu-doped zircon annealed at 1000°C are inconsistent with the zircon structure and suggest the formation of a ZrO₂-phase. The analysis of zirconium K-edge EXAFS of the ²³⁸Pu- and ²³⁹Pu-doped zircons annealed at 1200°C indicates highly crystalline zircon. However, the plutonium L_{III}-edge EXAFS of the ²³⁸Pu- and ²³⁹Pu-doped zircon annealed at 1200°C indicates the formation of both separated PuO₂ and the substitution of plutonium for zirconium in zircon structure. This result suggests that the solubility of plutonium in zircon at 1200°C is less than the 10 wt% that was originally incorporated in the zircon samples at 1465°C.

In collaboration with Drs. Ankudinov and Rehr at the University of Washington, the plutonium L_{III}-edge XANES has been modeled using FEFF8 and the atomic distributions based on the defect calculations discussed above. The experimental XANES of the unannealed zircons are well matched with the ab initio calculations based on the coupled substitution of two Pu³⁺ for two Zr⁴⁺ plus an oxygen vacancy in the zircon structure. The experimental XANES of the annealed zircons are best matched by the calculated XANES based on the PuO₂ structure. These results are consistent with those derived from the EXAFS calculations.

Gamma-Irradiation Studies

Temperature-controlled capsules have been used for irradiation studies within the PNNL (⁶⁰Co) gamma-irradiation facility. Samples of seven different glasses have been irradiated at four different temperatures (50, 100, 150, and 200°C) over the past two years. Glasses exposed to dose levels of about 2.5 x 10⁷ Gy and 7.5 x 10⁷ Gy at each temperature have been extensively characterized. Density measurements indicate no significant changes in volume. Raman, polarized Raman, UV-Vis-NIR, and FTIR spectroscopies have been carried out on these glass samples. Electron paramagnetic resonance (EPR) and transmission electron microscopy (TEM) characterization of these samples are planned. The highest dose glass samples, 1.5 x 10⁸ Gy, have just been removed from the gamma-irradiation facility for characterization. This dose is equivalent to about 25 years of storage time for DWPF glasses.

The Raman, polarized Raman, UV-Vis-NIR, and FTIR spectra from each of the glass compositions exhibit significant differences as a result of the chemical variation in the glass samples and the resulting effect on the silicate glass structure. However, initial spectroscopic analyses indicate only minor changes in the Raman, polarized-Raman, or FTIR spectra between the nonirradiated samples and those with 2.5 x 10⁷ Gy accumulated dose. Significant differences are observed between the nonirradiated samples and those with 2.5 x 10⁷ Gy and 7.5 x 10⁷ Gy accumulated dose in the 400 to 700 nm region of the UV-Vis-NIR optical absorption spectra of the sodium-borosilicate glass compositions. Furthermore, these radiation-induced variations display systematic dependencies on the irradiation temperature. At this time, the change in optical absorption in the 400 to 700 nm region are believed to originate from electronic defects, and D. Griscom (Naval Research Laboratory) will fully characterize the nature of these defects using EPR spectroscopy.

Electron and Ion Irradiation Studies

Amorphization in Zircon. Single crystals of synthetic zircon (ZrSiO₄) have been irradiated with different ions (from neon to bismuth) over a wide range of temperatures. The results of these studies (Weber et al. 1999), as illustrated in [Figure 4](#), show that amorphization in zircon is controlled by a variety

of parameters and is a more complex process than previously thought. The critical temperature (975K) for amorphization appears to be relatively independent of ion mass, and irradiation-induced decomposition is observed above this temperature (Meldrum et al. 1998), as indicated in Figure 4. The critical amorphization dose (in dpa) 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 dependence of amorphization due to α -decay events.

Amorphization in Pyrochlore Structures. The temperature dependence of the critical dose to completely amorphize $A_2Ti_2O_7$ pyrochlore structures (A=Y, Sm, Gd, Lu) under irradiation with 0.6 MeV Bi^+ ions is shown in Figure 5. 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 950K, the dose for amorphization rises rapidly as the rate of recovery becomes similar to the rate of amorphization. At room temperature, the dose to completely amorphize all the samples is on the order of 0.18 dpa.

Several $A_2Ti_2O_7$ pyrochlores were irradiated with 2 MeV Au^+ ions to produce a fully amorphous surface layer to depths of 300 to 400 nm. Leach testing (at pH 2) of as-prepared and irradiated samples was conducted to evaluate the effect of amorphization on dissolution rates and relative reactivities. The leach rates for the amorphous state of $Gd_2Ti_2O_7$ and $Lu_2Ti_2O_7$ were at least an order of magnitude higher than for the crystalline state. The increase in leach rate for $Y_2Ti_2O_7$ was less apparent, but the leach rate for the crystalline state of this composition is significantly higher (factor of 10) than for the crystalline

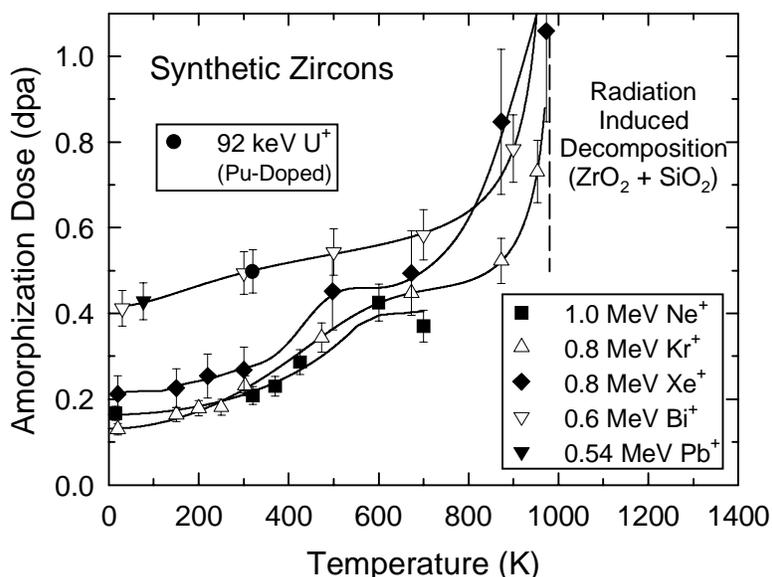


Figure 4. Temperature Dependence of Amorphization Dose in Zircon under Irradiation with Different Ions and from α -Decay in Plutonium-Doped Zircon (Weber et al. 1999). Also indicated is the radiation-induced amorphization that occurs above 950°C (Meldrum et al. 1998).

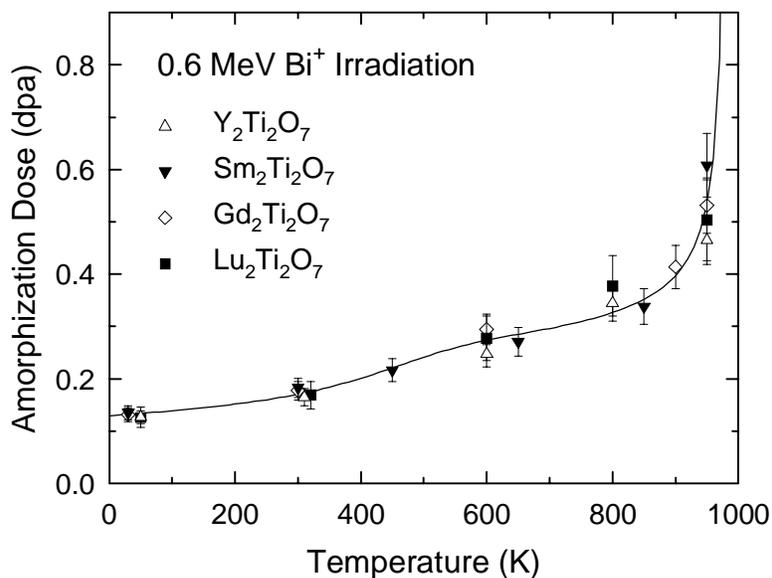


Figure 5. Temperature Dependence of Amorphization in Several Rare-Earth Titanates with the Pyrochlore Structure

state of either $Gd_2Ti_2O_7$ or $Lu_2Ti_2O_7$. For all three materials, the results suggest incongruent enhanced leaching of the gadolinium, lutetium, and yttrium relative to titanium. The measured order of magnitude increase in leach rate for the amorphous material relative to the crystalline material is consistent with the 20- and 50-fold increase in curium and plutonium release, respectively, measured in amorphous curium-doped $Gd_2Ti_2O_7$ relative to the fully crystalline state (Weber et al. 1985).

Bubble Formation in Glasses. Gas bubble formation in glasses has been studied in situ by ion implantation. Alkali silicate glass and sodium-borosilicate glass were implanted with 50 keV xenon ions at 200°C in a Hitachi-9000 electron microscope, and the formation of bubbles was studied by TEM during interruptions of the ion beam after discrete ion fluence steps. The results show that the alkali silicate glass has a larger volumetric swelling than sodium-borosilicate glass for the same implanted xenon ion fluence. The results also infer that xenon behaves like a perfect gas inside equilibrium bubbles. The difference in bubble growth in these two glasses is attributed to the difference in glass network structure.

Systematic studies of ion implantation in a simple sodium-borosilicate glass have been carried out using helium, krypton, argon, xenon, and oxygen ions. No oxygen bubbles were observed to form up to a fluence of 1×10^{17} ions/cm² during oxygen implantation; however, gas bubbles were observed for all the noble gas implantations. The average bubble size increased with atomic mass of the gas species. These results indicate that oxygen bubbles do not readily form for the simple sodium-borosilicate glass composition. This may be due to the large fraction of modifiers in this glass composition. Electron irradiation studies also showed no evidence of bubble formation in this glass composition, in agreement with the oxygen ion implantation study. This result, however, contradicts previous claims that electron irradiation can cause oxygen bubble formation in more complex glasses. One notable difference is that in the current studies under this project electrochemical polishing is used for sample preparation to avoid possible damage to the sample by ions; in previous studies, ion milling was used to prepare TEM samples.

Simultaneous electron irradiation during xenon ion implantation was found to increase the average bubble size in the sodium-borosilicate glass. This is attributed to ionization-enhanced diffusion and not to

any thermal effect. It is postulated that STEs generated by high-energy electron bombardment in the glass distort local structures and open channels for ion migration. Clusters that were observed in electron-irradiated glasses also indirectly support this speculation. Bubbles formed under only implantation with xenon implantation were observed to shrink when exposed to subsequent electron irradiation. There is no decrease in the xenon content in the samples, indicating that the xenon inside the bubbles diffused into the matrix but was not released from the samples.

Planned Activities

All the above research efforts will be phased out over the next few months as this project is terminated. As much work as possible will be brought to completion and written up for publication. Unfortunately, some of the most impactful work will neither be completed nor published. No follow-on funding has been identified at this time. Many team members will move on to other project or jobs. Samples will be temporarily archived in hopes that some of the needed additional studies can be funded in the future. Some of the computer simulation codes and expertise will find use under other projects. Other expertise and capabilities will be lost.

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