Project ID: **55367**

Project Title: **Investigation of Microscopic Radiation Damage in Waste Forms Using ODNMR and AEM Techniques**

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RESEARCH OBJECTIVE

This project seeks to understand the microscopic effects of radiation damage in nuclear waste forms. Our approach to this challenge encompasses studies of crystals and glass containing short-lived alpha- and beta-emitting actinides with electron microscopy, laser spectroscopy, and computational modeling and simulation. Much of our effort is to probe alpha-decay induced microscopic damage in 17-year old samples of crystalline yttrium and lutetium orthophosphates that initially contained ~1% of the alpha-emitting isotope Cm-244 (18.1 y half life). Studies also are conducted on borosilicate glasses that contain Cm-244, Am-241, or Bk-249, respectively. Our goal is to gain clear insight into accumulated radiation damage and the influence of aging on such damage, which are critical factors in the long-term performance of high-level nuclear waste forms.

RESEARCH PROGESS AND IMPLICATIONS

This report summarizes work after 2 years of a 3-year project. Using analytic electron microscopic and selective laser spectroscopic techniques, we first examined lanthanide orthophosphate crystals of $YPO_4$ and $LuPO_4$ that accumulated self-radiation damage from dopant (1 wt.%) $^{244}$Cm ions for 17 years. Although the accumulated dose of radiation (>$10^{18}$ alpha-decay events/mg) is significantly high, the samples that we examined physically remain crystalline on a macroscopic scale. Amorphization is not evident, even though isolated defects of various sizes were observed. Microscopic radiation effects in the crystals were manifested by (1) individual defect clusters of 2 to 5 nm size, which resemble disordered fission tracks, and (2) bubbles of 5 to 20 nm that are attributed to accumulation of He atoms generated during alpha decay events. These bubbles are relatively mobile and easily coalesce in electron microsocpy studies due to enhanced diffusion arising from electron irradiation. We have observed that, when exposed to an electron beam, the bubbles aggregated as a function of exposure time. This observation thus provides additional evidence that the bubbles developed from the aggregation of helium atoms that were created from alpha -decay of Cm-244, and the local lattice recovered from radiation damage. In addition to bubbles and fission tracks of nanometer sizes, there exist smaller scale structural defects and lattice strains that were revealed from selective laser excitation and fluorescence spectra. These defects are attributed to alpha-decay induced structural damage that occurred randomly throughout the lattice. Annealing of the samples at 773 K for 12 hours removed most of the residual defects.

Work by others has shown that lanthanide orthophosphates readily undergo amorphization by ion implantation. The lack of amorphization that we have observed in our studies of self-radiation damaged crystals suggests that, (1) recovery occurs simultaneously as damage is produced, and (2) the critical temperature of complete amorphization in the orthophosphate crystals is below room temperature for self-radiation damage induced by alpha decay. The critical temperature determined by ion implantation experiments for these materials is above room temperature. The difference in critical temperatures can be ascribed to the ionization annealing effects associated with the energetic alpha particles generated during alpha decay events. Also, because of the existence of slow annealing (tunneling) processes, the accumulated effects of self-radiation damage induced by radionuclides in waste forms over a long period of time may be different from those observed shortly after ion implantation.

Because of resistance to amorphization under self-radiation, lanthanide orthophosphates are very attractive materials for hosting high levels of long-lived radionuclides, such as Pu isotopes. However, aggregation and mobilization of bubbles might increase the leach rate of such radionuclides and influence the long-term stability of the waste forms. Theoretical modeling and molecular dynamics simulation of radiation-induced damage is being conducting in this project. Accomplishments in theoretical modeling include crystal field calculation for trivalent curium ions in disordered lutetium phosphate and yttrium phosphate lattices, and Monte-Carlo simulation of alpha-decay induced atomic position displacements (amorphization). Our results are consistent with the observations that much of the alpha-decay induced lattice damage has been reversed by self-annealing mechanisms.

Samples of borosilicate glass that contain natural uranium or short-lived actinide isotopes of Am-241, Cm-244, and Bk-249 were prepared as model waste forms and studied in this project with selective laser excitation and X-ray spectroscopy. Our studies have shown that, in borosilicate glasses, actinide ions have ordered structure as to their nearest neighbors. This property allows us to monitor radiation-induced structural damage. After preparation of the glasses samples, selective laser excitation was conducted to probe local environments of the actinide ions, and the same measurements were repeated 4-5 moths later. Extended X-ray absorption fine structure (EXAFS) spectra of the actinide ions in the glass samples also were recorded and analyzed in this project. Based on spectroscopic results, we have established a framework for analyzing radiation damage in this model waste form.

## PLANNED ACTIVITIES

During the remainder of this project, our effort in molecular dynamics calculation and simulation will be completed. We expect that this effort will provide a theoretical interpretation to the experimental results obtained in this project from studies on the lanthanide orthophosphates and, thereby, materially advance understanding of radiation damage effects in general. Variation in spectral properties, such as inhomogeneous line broadening in the borosilicate glass samples, will be probed periodically. These experimental data will be modeled in computational analyses that will provide a predictive understanding of the long-term effects of radiation damage in high level nuclear waste forms.

## INFORMATION ACCESS

G. K. Liu, J. S. Luo, S. T. Li, C.-K. Loong, M. M. Abraham, J. V. Beitz, J. K. Bates, and L. A. Boatner, *Scientific Basis for Nuclear Waste Management XXI*, MRS Sym. Pro. **V506**, 921 (1998).

G. K. Liu, S. T. Li, J. V. Beitz, and M. M. Abraham, J. Alloys & Compounds, **271/273**, 872 (1998).