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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 initial effort has focused on alpha-decay induced microscopic damage in 17-year old samples of crystalline yttrium and lutetium orthophosphates and thorium dioxide that initially contained ~1% of the alpha-emitting isotope Cm-244 (18.1 y half life) or the beta-emitting isotope Bk-249 (0.88 y half life). Studies will also be conducted on borosilicate glasses that contain Cm-244 or Am-241, 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 Progress and Implications

Amorphization previously has been thought to be the most important effect of radiation damage in crystalline and ceramic materials. Our studies show that for alpha-emitting actinide ions in certain crystalline phosphates, amorphization is not a significant effect of radiation damage. Instead, formation of microscopic cavities (bubbles) is an important consequence of alpha-decay events. This amorphization-resistant property makes orthophosphates a very attractive high level nuclear waste form. However, aggregation and mobilization of cavities (bubbles) might increase the leach rate of radionuclides and influence the long-term stability of the waste forms. Further research is needed before we can draw a final conclusion on the long-term effects of radiation damage in high level waste forms.

Our current understanding of microscopic effects of radiation damage is based on studies using analytical electron microscopy (AEM) and computer modeling of laser-induced optical spectra of phosphate samples doped with Cm-244.

Optical spectra of f-element ions in crystals provide "fingerprint" information about the local lattice structure, whereas line broadening of optical transitions between crystal-field states of different electronic multiplets within an f-configuration arises from static crystalline defects. We have developed a method for quantitative determination of local structure distortion from computer simulation of laser-induced fluorescence spectra. Crystal field spectra with resonant and non-resonant laser excitation were recorded for trivalent curium-244 ions in both lutetium and yttrium phosphate samples before and after annealing at 773 K for 12 hours. The observed inhomogeneous line width, 20 wave numbers, for both systems qualitatively indicates the absence of significant damage. In comparison, the inhomogeneous line width is typically about 200 wave numbers for trivalent Cm ions in glasses and less than 2 wave numbers in distortion-free crystals. After annealing, the inhomogeneous line width was reduced to less than 5 wave numbers which suggests that most lattice damage be removed.

Fundamental understanding of experimental results is achieved by theoretical modeling and computer simulation. Current accomplishments 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). Simulation of structural disordering and the observed inhomogeneous spectral line broadening show that, for most of the existing trivalent curium ions in the samples of Cm-244 doped lutetium phosphate and Cm-244 doped lutetium phosphate, the average displacements of lattice ions that surround a curium ion is only about 0.8 picometer which is 0.2% of the unit cell dimension. Based on the existing model of atomic displacement for alpha-decay induced damage, within 2 years after synthesis, the samples should be completely amorphized. Our results thus suggest that much of the alpha-decay induced lattice damage has been reversed by self-annealing mechanisms, which presently are not clearly understood.

Our AEM work on the same samples has produced consistent results and discovered a new phenomena technically more important than the amorphization effect. The electron diffraction (ED) patterns of the Cm-244 doped lutetium phosphate samples showed little evidence of crystalline amorphization. It was clearly evident in the high-resolution transmission electron microscopic (TEM) images of lutetium phosphate samples doped with 1% curium, that the lattice remained crystalline, however, numerous nanometer-sized (10-20 nm) bubbles were observed randomly embedded in the 17-year old samples. We have further observed that, when exposed to an electron beam, the embedded 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 amorphization.

Planned Activities

Imaging of damage annealing and bubble aggregation will be conducted using in-situ TEM and ED while a sample is heated in the electron microscope by the end of December, 1998. TEM images will be taken periodically from borosilicate glass samples that contain Am-241 or Cm-244 as radiation damage develops. High-resolution laser spectroscopic and ODNMR measurements will be conducted, before December 30, 1998, on other aged samples such as Cm-244 doped thorium dioxide to compare the effects of alpha-decay damage in different materials. Laser spectroscopic experiments will be conducted periodically on borosilicate glass samples that contain Am-241 and Cm-244 at various loadings to determine electronic and structural damage. Our theoretical modeling effort will focus on the mechanisms and their contributions to the room temperature annealing of amorphization that is evident in phosphate crystals that contain Cm-244. A microscopic mode will be developed for interpretation of our experimental results.

Other Access To Information

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)

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