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Radiation Effects in Nuclear Waste Materials

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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. The goal 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 plutonium, and other highly radioactive waste streams. A variety of experimental and computer simulation methods are employed in this effort. In general, research on glasses focuses on the electronic excitations due to ionizing radiation emitted from beta decay, since this is currently thought to be the principal mechanism for deleterious radiation effects in nuclear waste glasses. Research on ceramics focuses on defects and structural changes induced by the elastic interactions between alpha-decay particles and the atoms in the structure. Radiation effects can lead to changes in physical and chemical properties that may significantly impact long-term performance of nuclear waste materials. The current lack of fundamental understanding of radiation effects in nuclear waste materials makes it impossible to extrapolate the limited existing data bases to larger doses, lower dose rates, different temperature regimes, and different glass compositions or ceramic structures.

Research Progress and Implications

This report summarizes work after almost 2 years of a 3-year project. Work to date has resulted in 9 publications. Highlights of the research over the past year are presented below.

Theory, Simulations, and Modeling

A novel semiempirical methodology has been developed to model and simulate electron-hole pair formation in materials. This method determines the force contributions of the electron-hole pairs on the atoms and uses a time-dependent Hubbard model to propagate the electron-hole pair through the network. The model has been applied to crystalline and amorphous silicon and silica as test cases. In amorphous silica, the distorted bonds lead to localization of the exciton (formation of self-trapped exciton), and there is a significant amount of lattice relaxation. The force calculations indicate a preference for breaking bonds to form vacancy-interstitial pair defects, accompanied by large lattice relaxation effects. The pathways for the formation of various defects, using both the ground-state and excited-state forces and energetics, are being characterized. In addition, by coupling this methodology with other methods, it is possible to explore the formation and migration barriers of the defects. Initial calculations indicate that the migration barrier of a vacancy is lowered whenever an electron-hole pair interacts with the vacancy.

Threshold displacement energies and defect migration energies, which are not easily determined experimentally, are fundamental parameters controlling radiation effects in ceramics. Utilizing energy-minimization methodology, this project was the first to apply such methods to the determination of threshold displacement energies in ceramics, and the published results are in excellent agreement with experimental values. These methods have also been used to provide the only available estimates of displacement energies in zircon, since no experimental data are available. The recommended

values are being used by several groups in order to compare different irradiation data sets. This method has also been used to show that oxygen vacancy migration in zircon occurs with an activation energy of 1.3 eV by hopping between corners of nearest silica tetrahedra. The oxygen vacancy migration energy in pyrochlore ($Gd_2Ti_2O_7$) has also been determined and is in agreement with experimental data.

Dynamic and kinetic computer simulation techniques are being developed to study and model the fundamental processes of radiation effects in crystalline ceramics over broad time scales. A kinetic Monte Carlo (KMC) simulation code for zircon has been written, and it is presently being tested. In this code, the kinetics of individual defects hopping on each sublattice are followed. Cascades used as input to the KMC code currently come from binary collision simulations. A molecular dynamics simulation code for zircon is also being developed in parallel.

Experimental Studies

Seven different glass compositions have been irradiated at four different temperatures with gamma radiation to doses equivalent to 25, 75, and 100 MGy. Characterization has been performed only on the lowest dose samples. The intermediate dose samples were only recently removed from the gamma-irradiation facility, and the highest dose samples are continuing to be irradiated. Density measurements indicate no significant changes in volume after 25 MGy. Initial spectroscopic analyses indicate only minor changes in the Raman, polarized-Raman, and FTIR spectra due to irradiation. However, significant changes are observed in the UV-VIS-NIR optical absorption spectra of the sodium borosilicate glass compositions. These radiation-induced variations display systematic dependencies on the temperature at which the gamma irradiation occurred. At this time, the changes in optical absorption are believed to originate from electronic defects.

Density, stored energy, EXAFS, XANES, and diffuse x-ray scattering measurements have been performed on Pu-containing zircon and a suite of compositionally identical Pu-doped (1 wt.%) waste glasses prepared with different α -activities by varying the Pu (239/238) isotopic ratio. The stored energy measured in this glass composition nearly the largest ever measured in a nuclear waste glass and shows no evidence for saturation. This large stored energy may be due to the much lower dose rates in these studies and could provide a driving force for enhanced dissolution. In the glasses, cations with long cation-oxygen bonds show a greater sensitivity to radiation effects. In the fully amorphous Pu-239 zircon, long-range correlations are lost and the uranium daughter is in a highly disordered site that is not in thermal equilibrium. In both the fully amorphous zircon (Pu-238 samples) and in the fully crystalline zircon (Pu-239 samples), the Pu is present as Pu(III), as opposed to the expected Pu(IV) state, and resides in a site that is very similar to $PuSiO_4$, the plutonium analog of zircon. This valence state for Pu in the zircon samples is most probably due to the reducing conditions employed during the original sintering.

The temperature dependence of amorphization in zircon and pyrochlore ($Gd_2Ti_2O_7$) under irradiation with different ion species has been determined. It was also found that ion-beam-induced recrystallization of fully amorphous pyrochlore occurs at 800° C under 1 MeV Kr^+ irradiation. Indentation measurements of pyrochlore irradiated with 4 MeV Au ions indicate a 15% decrease in elastic modulus and a 42% decrease in hardness. The accumulation and recovery of ion-beam-induced disorder in $SrTiO_3$ has also been studied by ion channeling methods. Preliminary analysis indicates that the total defect concentration on the Sr and Ti sublattices exhibits an exponential dependence on the annealing temperature. The recovery processes for defects on the O sublattice appear to be faster.

The mechanisms of gas bubble formation in nuclear waste glasses are being investigated by irradiation with inert gas atoms (50 keV Xe) at temperatures between 200 and 600° C. Modeling of data suggests that recoil-resolution of gas atoms from bubbles plays an important role in bubble growth. As the implantation dose increases, bubbles grow by random gas accumulation until nearby bubbles interact and coalesce. The results also indicate that intermittent exposure to ionizing electrons retards bubble growth. A decrease in the threshold dose for bubble formation with increasing temperature indicates increasing Xe and bubble mobility.

Since single crystals of many oxides of interest are not readily available, the growth of single crystals or single crystal films has become necessary. Epitaxial films of pyrochlore ($Gd_2Ti_2O_7$) have

been successfully grown, and ion-channeling measurements indicate excellent crystallinity. A x-ray diffraction system has been installed on the target chamber at the LANL ion-beam facility to provide a unique new capability for in situ investigations of ion-irradiation induced structural changes in solid matter.

Planned Activities

A paper describing the novel semiempirical methodology to model and simulate electron-hole pair formation in materials will be prepared and submitted for publication. Later this Summer, the modeling effort will begin simulations of excitons in binary silicate materials and on the energetics and dynamics of the triplet and singlet states of excitons in silica glass. Threshold displacement energies and defect migration energies will be determined for $Gd_2Ti_2O_7$. MD simulations of damage processes from displacement cascades in zircon will begin this Summer. In early FY 1999, parameter variation studies using the KMC code for zircon will be initiated to assess the reasonableness of the present simple model relative to a range of values expected for defect migration energies.

Characterization of glass samples irradiated with gamma radiation to 75 MGy will be initiated in June 1998. The higher dose samples will be removed for testing in November 1998 after receiving a dose of 150 MGy. In addition to characterization already performed, electron paramagnetic resonance (EPR) and transmission electron microscopy characterization will be performed.

In June/July of 1998, the Pu-zircons will be heat treated in air at elevated temperatures ($\sim 1500^\circ C$), and EXAFS/XANES measurements will be performed to confirm oxidation of the Pu(III) to Pu(IV). Additional analyses on the diffuse scattering data will be completed by October 1998, and the results will be submitted to a journal for publications.

Studies of defect accumulation and amorphization will be initiated on $Gd_2Ti_2O_7$ single crystal films and on polycrystalline $Gd_2Zr_2O_7$ in August 1998. Studies of defect recovery and ionization-enhanced recrystallization will be initiated on $SrTiO_3$ at the same time. Studies of helium and oxygen bubble formation in glasses will be initiated in July 1998.

Other Access To Information

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