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Radiation stability test on multiphase glass ceramic and crystalline ceramic waste forms

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ABSTRACT

A radiation stability study was performed on glass ceramic and crystalline ceramic waste forms. These materials are candidate host materials for immobilizing alkali/alkaline earth (Cs/Sr-CS) + lanthanide (LN) + transition metal (TM) fission product waste streams from nuclear fuel reprocessing. In this study, glass ceramics were fabricated using a borosilicate glass as a matrix in which to incorporate CS/LN/TM combined waste streams. The major phases in these multiphase materials are powellite, oxyaptite, pollucite, celsian, and durable residual glass phases. Al_2O_3 and TiO_2 were combined with these waste components to produce multiphase crystalline ceramics containing hollandite-type phases, perovskites, pyrochlores and other minor metal titanate phases.

For the radiation stability test, selected glass ceramic and crystalline ceramic samples were exposed to different irradiation environments including low fluxes of high-energy (~1–5 MeV) protons and alpha particles generated by an ion accelerator, high fluxes of low-energy (hundreds of keV) krypton particles generated by an ion implanter, and *in-situ* electron irradiations in a transmission electron microscope. These irradiation experiments were performed to simulate self-radiation effects in a waste form. Ion irradiation-induced microstructural modifications were examined using X-ray diffraction and transmission electron microscopy. Our preliminary results reveal different radiation tolerance in different crystalline phases under various radiation damage environments. However, their stability may be rate dependent which may limit the waste loading that can be achieved.

1. Introduction

Exploration of options for reprocessing of used nuclear fuel remains of interest despite the current prevalence of a 'once-through' fuel cycle terminated by eventual geologic repository storage. A once-through fuel cycle means that the fuel experiences a single pass through a reactor after which it is packaged and becomes high-level waste (HLW), disposed of in a repository. Through the Fuel Cycle Research and Development (FCR&D) Program, the Department of Energy, Office of Nuclear Energy, is currently evaluating the modified-open nuclear fuel cycle to increase the efficiency of nuclear power production and reduce the amount of HLW. In the modified-open nuclear fuel cycle, the vast majority of the used fuel can be recycled, used for new fuel bundles, and sent back through a nuclear reactor. The envisioned fuel reprocessing technology would separate the fuel into several fractions, thus, partitioning the waste into groups with common chemistries. With these partitioned waste streams, it is possible to treat waste streams separately or combine waste streams for treatment when it is deemed appropriate. A portion of the fission products generated during burn up in a nuclear reactor are nonfissionable and, once separated from the fissionable material, must be immobilized in stable waste forms. The nonfissionable products targeted for an oxide waste form are in the following three waste streams generated with the projected transuranic extraction (TRUEX$^+$) process: alkalis/alkaline earths (CS representing ^{137}Cs and ^{90}Sr), lanthanides (LN), and transition metals (TM).

Multiphase borosilicate glass ceramics are one candidate waste form for immobilizing the combined CS+LN+TM-fission products [1,2]. Unlike borosilicate glass alone, which offers many favorable characteristics but suffers from low waste loading and potential issues stemming from low glass transition temperatures [3,4], glass-ceramic waste forms have the potential to provide both significantly higher waste loading and enhanced mechanical integrity due to the presence of crystalline phases [5]. The former benefit is

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realized through designed crystalline phases grown during fabrication that immobilize elements that have low solubility in the glass phases. In the absence of such intentionally engineered phases, certain elements, most notably molybdenum and select lanthanides, will precipitate as various unwanted phases during the fabrication process or over time under storage and can appreciably degrade performance of the waste form [6–9].

Crystalline ceramic materials for HLW immobilization are another option [10–13]. Titanate ceramics have been thoroughly studied for use in immobilizing nuclear wastes (e.g., the SYNROC family) due to their natural resistance to leaching in water [11,12]. Assemblages of several titanate phases have been successfully demonstrated to incorporate radioactive waste elements, and the multiphase nature of these materials allows them to accommodate variation in the waste composition [13]. While these materials are typically densified via hot isostatic pressing, recent work has shown that they can also be produced from a melt process analogous to glass ceramic material processing. This production route is advantageous since melters are already in use for commercial and defense HLW vitrification in several countries, and melter technology greatly reduces the potential for airborne contamination as compared to powder handling operations.

The stability and durability of the vitrified waste forms need to be systematically investigated in order to assess their viability. This study focuses on radiation stability of waste forms made from both glass and crystalline phases. Most of the self-radiation in a waste form incorporating fission products is due to beta particle and gamma emission [14,15]. These emissions cause radiation damage primarily via radiolytic processes, because both beta and gamma particles induce substantial electronic excitations in a target material. Experimental techniques to examine radiation damage include: (1) Characterizing samples taken from reactors or other facilities (e.g., irradiated *in situ* by the full spectrum of radiation: neutron, α, β, and γ); (2) Characterizing samples irradiated by ion accelerator *ex situ*; (3) Irradiating samples in a transmission electron microscope (TEM) using high-energy electrons to simulate radiolysis effects; (4) Incorporating radionuclides into the material during processing whose radiation causes *in situ* or self-radiation.

Preliminary evaluations of the radiation stability of select glass ceramic and crystalline ceramic waste forms were undertaken by subjecting samples to ion irradiations at the Ion Beam Materials Lab (IBML), and *in-situ* electron irradiation in a TEM at the Electron Microscopy Lab (EML), Los Alamos National Laboratory (LANL). Light and heavy ion bombardment, and electron irradiations are used to simulate the self-radiation damage that occurs in a material incorporating nuclides undergoing radioactive decay. Light ions and electrons provide a useful means to examine radiolysis effects because they deposit nearly all of their energy in solids via electronic loss processes; heavy ions are used to simulate energetic recoil nuclei interaction which involves ballistic processes.

2. Experimental

The glass ceramic and crystalline ceramic waste forms were prepared at Pacific Northwest National Laboratory (PNNL) and Savannah River National Laboratory (SRNL) as reported previously [1,2,10]. The select samples were cut into pieces and polished with alumina lapping films (down to 1 μm) to obtain a mirror finish for further investigation. In preparation for ion irradiation, all samples were finally polished with a 40 nm colloidal silica slurry (Syton HT50, DuPont Air Products NanoMaterials L.L.C, Tempe, AZ), in order to remove the surface damage created by the previous mechanical polishing steps.

Ion irradiation experiments were performed at room temperature (~300 K) at IBML, using a 200 kV Danfysik high current research ion implanter and a 3.2 MeV Tandem accelerator. 600 keV Kr, 5 MeV alpha (He), and 2 MeV proton (H) beams were used in this study to evaluate radiation stability in these waste form materials. The Stopping and Range of Ions in Matter (SRIM) program [16] was used to estimate radiation dose in ion irradiated samples. A threshold displacement energy of 40 eV (this is an arbitrary assumption) was used for all target elements. Fig. 1 shows the results of this simulation for these compounds. The peak displacement damage dose for 600 keV Kr irradiation (Fig. 1(a)) is ~3.5 dpa at a fluence of 2.5×10^{19} Kr ions/m^2; the peak radiation dose for 5 MeV He irradiation $\sim 8 \times 10^9$ Gy at a fluence of 1×10^{21} He ions/m^2, and 8×10^9 Gy for 2 MeV H at a fluence of 4×10^{21} H ions/m^2 in Fig. 1(b).

For the *in-situ* electron beam irradiation study, a TEM specimen was prepared in plan-view geometry. This plan-view sample was

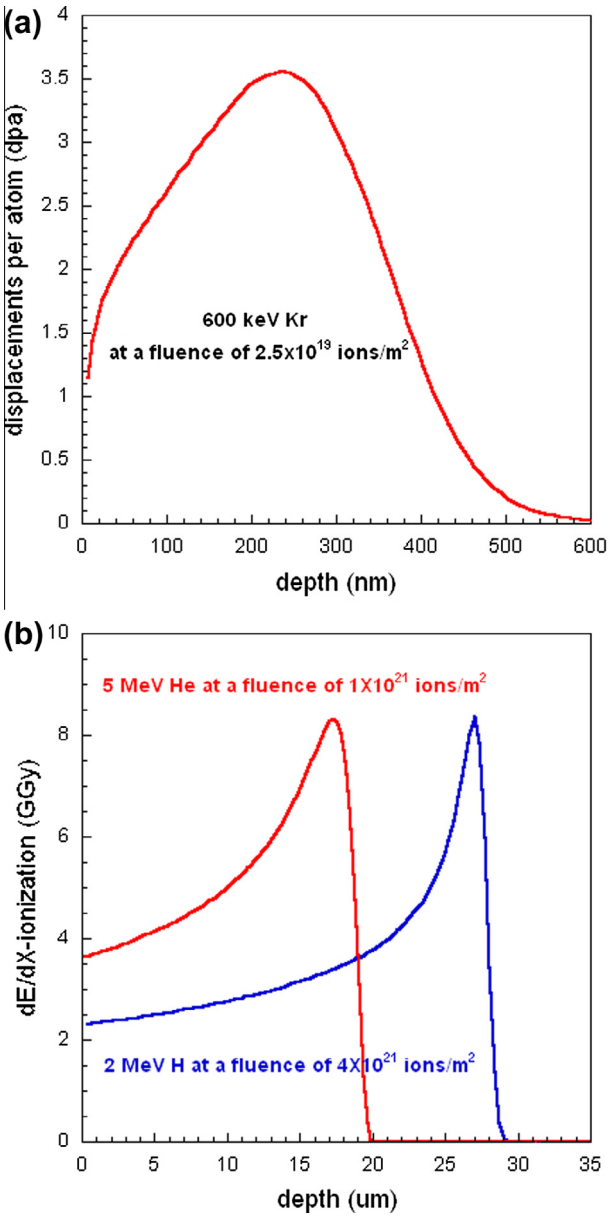

Fig. 1. (a) SRIM simulation results showing the radiation damage dose profile as a function of depth for 2 MeV H and 5 MeV He ion irradiation of a glass ceramic to a fluence of 4×10^{21} H/m^2, and 1×10^{21} He/m^2, respectively. (b) The displacement damage profile as a function of depth for 600 keV He ion irradiation of a glass ceramic to a fluence of 2.5×10^{19} Kr/m^2.