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Project Title: **Distribution & Solubility of Radionuclides & Neutron Absorbers in Waste Forms for Disposition of Plutonium Ash & Scraps, Excess Plutonium, and Miscellaneous Spent Nuclear Fuels**

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Distribution and Solubility of Radionuclides and Neutron Absorbers in Waste Forms for Disposition of Plutonium Ash and Scraps, Excess Plutonium, and Miscellaneous Spent Nuclear Fuels

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Research Objective

The objective of this research is to develop a basic understanding of the distribution and solubility of radionuclides and neutron absorbers in waste forms and their release from waste forms by studying the local structural environments of these constituents in representative materials.

Research Statement

Crucial to the near-term DOE/EM mission of developing waste forms for the disposal of specific plutonium-containing wastes is a fundamental understanding of the radionuclide and neutron absorber solubility in glasses and ceramics. This understanding is empirically based, making it difficult to provide a defensible position on issues such as waste-form selection and development, assessment of waste form criticality safety, stability, long-term performance, and waste-form qualification for repository acceptance. The elucidation of the fundamental relationship between the local structure of radionuclides and neutron absorbers and their solubility in waste forms will advance material science and provide depth to the defense.

Research Progress

Introduction

We have been examining the solubility of surrogate oxides in a suite of baseline glasses that allow us to vary the glass melt chemistry. Over the past year, we have found evidence to suggest that the solubility of metal oxides in sodium boro-aluminio-silicate glasses is facilitated by the formation of nanometer heterogeneities that we refer to as “clusters” of the metal-oxide moiety. We are uncertain as to the exact composition of these clusters, but they appear to be rich in the metal being dissolved. In this report, we discuss the results from several spectroscopic techniques. The presence of clusters appears to be pervasive from very low metal oxide concentrations and appears to be a metastable condition for the metal oxide.

We have also examined uranium- and plutonium-containing glasses and found that the oxidation state has an important effect on the solubility with the lower oxidation state of plutonium being more soluble. Crystalline waste forms too have been investigated. Here, again, the oxidation state of the surrogate metal plays an important role. We have looked at the crystal chemistry of pyrochlore, zirconolite, and perovskite.

We discuss the baseline glasses that we reported last year and the new glasses that we made this year. We then discuss our results for gadolinium and hafnium glasses, followed by a discussion of the nuclear magnetic resonance (NMR) and transmission electron microscopy (TEM) results. We then discuss our results from our investigations of the uranium- and plutonium-containing glasses. We finish with a discussion of crystalline materials as potential waste forms.

Glasses Studied

Baseline Glasses

The compositions of the baseline glasses[1] are designed according to a simplified Pu16MC3 sodium-alumino-borosilicate glass developed for plutonium immobilization (Darab et al. 1997). More complicated baseline glasses are used in our uranium and plutonium studies (Feng et al. 1998). Normally, baseline glasses were prepared from well-mixed oxide and carbonate powders. Radionuclide surrogates (HfO_2, Gd_2O_3, La_2O_3, Nd_2O_3) and neutron absorbers (HfO_2 or Gd_2O_3) were then added to ground baseline glasses and melted at 1450-1560°C. The melt was quenched in water. Resulting glasses or glass-crystal mixtures were analyzed with different techniques to develop an understanding of the solution mechanisms.

Clear glasses resulted from the melting of the majority of the baseline compositions at or below 1450°C. Glasses did not form from compositions such as PA0, PB0, PC0, and PA20, below 1450°C. However, glasses could be formed when surrogate oxides were added to the melt. Characterization of the baseline glasses has been carried out with NMR on $60SiO_2$-aB_2O_3-bNa_2O-cAl_2O_3 glasses and TEM on the B20 baseline glass.

Rare Earth Element Solubility in Glasses

We reported Gd_2O_3 solubilities in $60SiO_2$-aB_2O_3-bNa_2O-cAl_2O_3 baseline glasses in our last annual report. Recently, we found that the solution behavior of La_2O_3 in the baseline glasses is very similar to that of gadolinium. A study of the La_2O_3 solubility was needed because we could not analyze gadolinium-containing glasses with NMR (gadolinium has a strong magnetic moment). Our results show that there is a one-for-one substitution of La_2O_3 for Gd_2O_3 in both the glass and the crystals that precipitate from the glass melt. A complete solid solution was observed in the B15 glass for the system $Na_{1-x}(Gd, La)_{9+x/3}Si_6O_{26}$ ($0<x<1$).

Our results indicate that there is a small temperature dependence of the Gd_2O_3 solubility. Between 1400°C and 1550°C, the Gd_2O_3 solubility in the B15 glass increases less than 7 mass%. Our results indicate an enthalpy change of Gd_2O_3 dissolution in this baseline glass is about 40 kJ/mol.

Figure 1 shows Gd_2O_3 ($GdO_{1.5}$) solution behavior in $60SiO_2$-$15B_2O_3$-xNa_2O-$(25-x)Al_2O_3$ glass system. Similar results were found for La_2O_3 and Nd_2O_3, which indicates that they have similar solubility. The Gd_2O_3 solubility changed rapidly with the $Na_2O/(Na_2O + Al_2O_3)$ ratio in the glass. At $Na_2O/(Na_2O + Al_2O_3)$ equal to 0.50, its solubility reaches a minimum. As the $Na_2O/(Na_2O + Al_2O_3)$ ratio increases from 0.50 to 1.00 or decreases from 0.50 to 0, Gd_2O_3 solubility increases from 5 to 46 and from 5 to 63 mass%, respectively. When $Na_2O/(Na_2O + Al_2O_3)$ is ≤ 0.35, Gd_2O_3 additions to the baseline glass aid glass formation. In this case, there are two solubility limits a lower and an upper.

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[1] Glasses are labeled and named in the following fashion: in the system $60SiO_2 \cdot aB_2O_3 \cdot bNa_2O \cdot cAl_2O_3$ where a = 5 to 20; b = 10 to 30; c = 2 to 15; glass B15 has a = 15, b = 20, and c = 5; in the system $60SiO_2 \cdot 15B_2O_3 \cdot xNa_2O \cdot (25-x)Al_2O_3$, x was varied from 0 to 25 and designated PLr, PAr, PBr, and PCr, where $r = Na_2O/(Na_2O + Al_2O_3)$; in the system $\alpha SiO_2 \cdot \beta Na_2O \cdot \gamma Al_2O_3$, α was varied from 38.33 to 66.67, β 15 to 33.33, and γ 0 to 46.67.

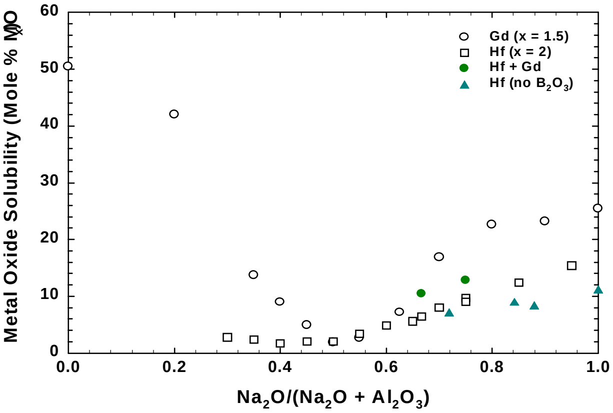

Figure 1. The Dependence of Gadolinium and Hafnium Oxide Solubility on Glass Composition

The lower solubility limit is defined by the existence of mullite ($Al_6Si_2O_{13}$, ideal formula). Increasing the Gd_2O_3 causes mullite to dissolve. The lower solubility decreases from 28 to 0 mass% as $Na_2O/(Na_2O + Al_2O_3)$ increases from 0 to 0.35. For $Na_2O/(Na_2O + Al_2O_3)$ between 0 to 0.20 and 0.70 to 1.00, $Na_{1-x}Gd_{9+x/3}Si_6O_{26}$ (x=0 to 1) crystals (upper solubility) and mullite [$(Al_4SiO_8)_{1.2}$ (formula for XRD), lower solubility] were identified with XRD. For $Na_2O/(Na_2O + Al_2O_3)$ in range 0.35 to 0.625, the glasses exhibit opalescence, indicating liquid-liquid phase separation. When examined in the TEM, the average size of the dispersed phases was about 50 nm. We found that the dispersed phase was gadolinium rich compared with the continuous phase. Another much smaller dispersed phase (several nm) was found for both in the liquid phases.

In the B20 glass, as the concentration of Gd_2O_3 increases from 0 to 47 mass%, the glass density increases from 2.4 g/cm^3 to 3.7 g/cm^3. We used the density, composition, and published ionic radii to calculate the vacancy volume for each glass. The vacancy volume reaches a maximum when Gd_2O_3 concentration is about 5 mass%. Further increasing the Gd_2O_3 concentration causes the vacancy volume ration to decrease. This has implications about the structure surrounding the gadolinium. These samples were also studied with laser-induced, time-resolved fluorescence spectroscopy and lifetime measurement. The intensity of the emission bands was found to increase from 1 to 20 mass% Gd_2O_3 and then to decrease at higher Gd_2O_3 concentrations. In parallel, the fluorescence lifetime decreased rapidly when the concentration of Gd_2O_3 was greater than 20 mass%. This indicated that a significant decrease in Gd-Gd distance occurred. Under TEM, we observed that a small dispersed phase, as seen in the phase-separated glasses discussed above, increased as the Gd_2O_3 concentration increased.

In our efforts to find another spectroscopic tool to examine the nature of these gadolinium-containing clusters, we determined that small additions of Nd_2O_3 for Gd_2O_3 could be used as a probe of the gadolinium site(s). The presence of Nd_2O_3 in these glasses allows us to use UV-Vis spectroscopy to examine these glasses. While the resulting spectra are complex, there is one peak that is uncomplicated, i.e., it appears to be a single peak whereas the others appear to be composed of several overlapping peaks. We are able to see some differences in the peak position and the maximum width at half height. We are still trying to interpret these data. The solubility behavior of Nd_2O_3 is similar to that observed for Gd_2O_3 and La_2O_3.

Glasses B20La5, B20La20, and B20La47 (peralkaline) were analyzed with ^{11}B and ^{27}Al solid-state nuclear magnetic resonance (NMR). In all of these glasses, the aluminum occurs in predominantly four-fold (tetrahedral) coordination, while boron occurs as a mixture of three-fold (trigonal planar) and four-fold (tetrahedral) coordinated species. It was found that, as more La_2O_3 was added to the B20 base glass, the boron environment became more three-fold coordinated.

Hafnia Solubility in Glasses

Solubility studies of HfO_2 in sodium boro-alumino-silicate glasses have been extended from the peralkaline [$Na_2O/(Na_2O + Al_2O_3) > 0.5$; molar ratio] to the peraluminous [$Na_2O/(Na_2O + Al_2O_3) < 0.5$] compositional range (Figure 1). Optical microscopy, scanning electron microscopy (SEM), NMR, and x-ray absorbance fine structure (EXAFS) have been used to document morphological, mineralogical, compositional, and atomic-level structural differences for the glasses. Results from electron microprobe quantitative microanalyses of selected HfO_2 glasses compare favorably with our target glass compositions. These results also confirm that sodium was lost during the preparation of high Na_2O-containing glasses. Four sodium alumino-silicate glasses without boron have been prepared to help elucidate the role of boron in HfO_2 solubility. We also prepared mixed Gd_2O_3-HfO_2 glasses to evaluate the possible competition between the two absorbers/surrogates.

Hafnia (HfO_2) has been identified as a precipitate in both peralkaline and peraluminous glasses with x-ray diffraction (XRD). The only other crystalline phase found is mullite, and it occurs only in peraluminous glasses and in Na10Gd2Hf19. Hafnia in peraluminous glass occurs as pinacoidal prismatic crystals that are compositionally zoned or twinned with sections that are mainly HfO_2 and others that contain hafnium, aluminum, oxygen, and perhaps sodium. Only a limited number of peraluminous glasses could be made (Figure 1) because these compositions could not be melted at the upper limit of the furnace (1600°C). In the peralkaline glasses, crystals are also zoned or twinned, but with respect to hafnium, silicon, sodium and oxygen, not aluminum: one sector is essentially hafnia, while the other that appears epitaxial contains little hafnium and significant silicon and sodium.

We have performed TEM analyses on three Na10Hf10 glasses, homogenized for one, three, and seven hours, and for the B20 glass series, homogenized for two hours. There appears to be a similarity between B20 glasses with varying amounts of HfO_2 and Na10Hf10. All samples examined exhibit a similar feature: light and dark “spots,” approximately 5 nm in diameter, randomly but seemingly homogeneously distributed throughout the material studied. As with the gadolinium-containing glasses, we have tentatively identified these as clusters. The density of the clusters does not seem to change with increasing HfO_2 content, although a more rigorous examination is needed. Some of our results (see the discussion below) suggest that the hafnium-containing clusters may be compositionally different than the gadolinium-containing clusters. Stereoscopic TEM photographic pairs from the gadolinium-glasses illustrate that the clusters are spherical and separated. They occur throughout the glass volume. Results from our TEM examination of the glasses annealed for various durations indicate that the grains of HfO_2 are residual from the glass batch. The existence of the clusters persists throughout the annealing. Our TEM analyses also show that the glasses are inhomogeneous with respect to hafnium. Locally, energy dispersive spectroscopy (EDS) of B20Hf5 (5 mass% HfO_2) gives a scaled hafnium peak area very similar to that for B20Hf31 (31 mass% HfO_2). The composition and structure of the clusters remains to be determined.

Analyses with EXAFS spectroscopy have been completed, and the data have been modeled successfully for two series of glasses. We examined the effect of changing HfO_2 content with the series Na10Hf5 through Na10Hf20 (10 mol% Na_2O, 5 to 20 mass% HfO_2). We looked at the effect of changing the $Na_2O/(Na_2O + Al_2O_3)$ while holding B_2O_3 and SiO_2 in the same molar proportions. The EXAFS data indicate a distinct difference between peralkaline and peraluminous glasses, with the sample representing the boundary between the two compositional ranges [$Na_2O/(Na_2O + Al_2O_3) = 0.5$] being distinct from or intermediate between the others. Changes in the calculated hafnium coordination are found as the boundary is crossed. While these data are preliminary, they indicate that the hafnium in peraluminous glasses has oxygen near neighbors and oxygen and aluminum as next nearest neighbors. On the other hand, the peralkaline glasses are best modeled without aluminum as next nearest neighbors. None of the XAFS spectra from the glasses resemble HfO_2

(actual) or $HfSiO_4$ (simulated) reference spectra.

Glasses Na10Hf5 through Na10Hf20 (peralkaline), and PL50Hf6 through PL30Hf8 (peraluminous) have been examined with solid-state NMR (^{11}B, ^{27}Al). The preponderance of aluminum is in four-fold coordination for both peraluminous and peralkaline glasses, while the boron coordination is a mixture of three-fold (trigonal planar) and four-fold (tetrahedral). In general, it was found that peraluminous glasses contain far less boron in tetrahedral coordination than in trigonal coordination, whereas the opposite is true for peralkaline glasses. In both the Na10 series and Na30 series peralkaline glasses, the boron coordination changes similarly with the addition of hafnium: the more HfO_2 added to the same base glass, the more three-coordinate boron is found.

Interpretation of Solubility, NMR, and EXAFS Data

For the Na10 and Na30 peralkaline glass series, the boron environment was found with NMR to become more three-fold coordinate with increasing additions of HfO_2. Likewise, for the B20 peralkaline glass series, the boron environment was also found to become more three-fold coordinate with increasing additions of La_2O_3. As association of sodium with the boron is required to maintain the boron in four-fold coordination, an immediate conclusion one might be tempted to draw from these results is that Hf(IV) or La(III) require some sort of association with sodium during the dissolution process and that Hf(IV) and La(III) compete more strongly for the available sodium than does boron. Hence, as more HfO_2 or La_2O_3 is added, sodium that in the absence of these oxides, would stabilize four-coordinate boron, instead aids in the dissolution of Hf(IV) or La(III) and the boron becomes more three-fold coordinate. One might also contend that some equilibrium might eventually be reached where the boron will not give up any more sodium to the Hf(IV) or La(III) and the solubility limit of the system is reached.

If the above model were true, however, the solubility limit of HfO_2 in these glasses should increase with increasing "free sodium." The free sodium is the total sodium in the glass minus the concentration of aluminum, which very strongly achieves four-fold coordination by association with sodium, minus the concentration of four-fold coordinated boron at equilibrium. Thus, glasses with no aluminum or boron and high concentrations of sodium (e.g., NaSiO-X) should show maximum HfO_2 solubility. As a matter of fact, the NaSiO-X along with the other glasses with no boron, in spite of their high concentrations of "free sodium" exhibit less-than-expected HfO_2 solubilities (Figure 1).

Thus, we believe that the boron is playing an important role in the dissolution of the HfO_2, perhaps by allowing a more energetically favorable route through which sodium can become associated with Hf(IV). We are currently developing chemical equilibrium-based models to calculate the solubility of HfO_2 from the relative amounts of B_2O_3, Al_2O_3 and Na_2O in these glasses.

As the composition of the base glass approaches that where the concentration of Na_2O and Al_2O_3 are equal, i.e., the boundary between peralkaline and peraluminous regions, the concentration of free sodium approaches zero. At this point, regardless of the mechanism by which sodium could become associated with Hf(IV) there is little free sodium and the solubility of HfO_2 approaches a minimum.

Finally, in the peraluminous region, there is less Na_2O than Al_2O_3 and it is difficult to maintain four-fold coordinate aluminum. Theoretically then, NMR characterization of peraluminous glasses containing, for example HfO_2, should indicate that the aluminum environment becomes more six-fold coordinate as more Na_2O is removed. In actuality, the NMR results show that the aluminum environment maintains four-fold coordination and there is very little four-fold coordinated boron in the hafnium-containing peraluminous glasses. Additionally, the EXAFS results indicate that aluminum is associated with the hafnium as a second nearest neighbor. One interpretation is that, in order to maintain four-fold coordination, one or more aluminum become associated with a Hf(IV) as more sodium is removed in the peraluminous region. This would explain the NMR data, the EXAFS data, and the increase in HfO_2 solubility, as more Na_2O is removed in peraluminous glass compositions.

Since the trends in solubility for HfO_2 and for $(La/Gd/Nd)_2O_3$ are similar, but different in magnitude, perhaps similar mechanisms with different equilibrium constants can be used to describe the solubilities of these and other types of cations (such as actinides or other troublesome transition elements) in glass.

Microprobe Analyses

Electron microbeam techniques, such as electron microprobe analysis (EMPA), backscattered electron (BSE) EDS, and x-ray mapping, have been used to characterize distributions of each individual element and actual contents of elements in the glass products. The gadolinium- and hafnium-glasses studied are homogeneous in composition except for the sample containing a precipitated gadolinium-bearing crystal phase. Good agreement was obtained between the analyzed compositions and the target compositions. The gadolinium-containing crystals took more gadolinium from the glass matrix and made it heterogeneous in composition.

In the gadolinium-containing glass that is above saturation, the separated crystals are up to 200 µm in length. Backscattered electron images of the samples showed that the crystals are elongated, acicular, prismatic, or dendritic. Cross-sections of the crystals are often hexagonal, sometimes with hollow hexagonal features (Figure 2). The different shapes of the crystals indicate that they were probably formed during the different stages of crystallization as the glass cooled. Chemical compositions of precipitated crystals are more enriched in gadolinium than in the glass matrix. Crystals of different shapes have the same composition, and each crystal is homogeneous in composition. The composition of the crystals is consistent with the XRD results described above. The glass composition near the precipitated crystals was depleted in gadolinium and richer in the other glass components. This is consistent with the composition of the crystals.

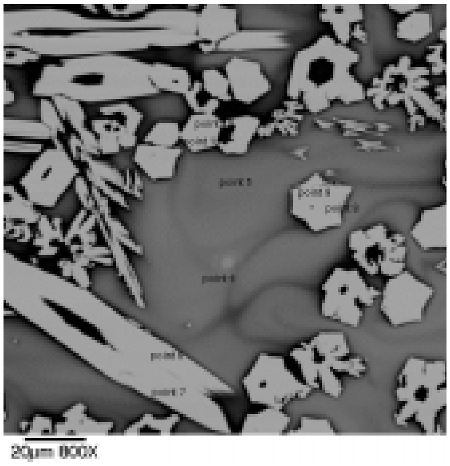

Figure 2. Backscattered Electron Images of the Crystalline Phase in the Gadolinium-Containing Glass Matrix

Solubility and Local Structure of Uranium in Silicate Glass

A standard soda-lime silicate, SRM 1830, was obtained from National Institute of Standards and Technology and selected for our studies of the uranium solubility and local structure under oxidizing and reducing conditions. This glass contains (in mass%) 73.1 SiO_2, 13.8 Na_2O, 8.6 CaO, 3.9 MgO, 0.1 Al_2O_3, 0.1 Fe_2O_3, plus small quantities of K_2O, TiO_2, and SO_3. This glass was selected for its good chemical durability and its relatively high concentration of Na_2O. The high Na_2O favors high uranium solubility.

The uranium solubility study was previously summarized (Feng et al. 1998). The results are briefly summarized here: under oxidizing conditions, the solubility was 30 mass% UO_3 at 1500°C based on optical, XRD, and TEM studies. At 31 mass% UO_3 and above, uranium crystallizes as U_3O_7 in the oxidized glasses. Under reducing conditions, the solubility was less than 30 mass% and UO_2 precipitated.

The XAFS have been collected on these glasses at room temperature at the Stanford Synchrotron Radiation Laboratory. The U L_{III} near edge of the oxidized and reduced glasses doped with uranium was reported (Feng et al. 1998). From these analyses, we determined that, on the average, U(V) was present in oxidized glasses above 10 mass% and U(IV) in reduced glasses. The axial and equatorial U-O parameters can be derived, but the extraction of the structural parameters beyond these shells, except for the identification of U-U scattering, which is clearly evident in some of the U40 materials (~4Å), is not practical. The respective trends in coordination number and bond distances with increasing uranium content are consistent prior to formation of U(IV).

The bond-valence model (Brese and O'Keefe 1991) was use to calculate the valence from the U-O bond distance and U to O coordination number. Good agreement was found suggesting the majority of the U is U(VI) in the oxidized glasses, with 10 and 20 mass% UO_3 and U(IV) in the reduced glasses. The bond-valence model results further suggest a trend that U(V) increases as UO_3 increases above 20 mass% in the oxidized glasses. Combining the uranium solubility data with results of the XAFS, bond-valence model, XRD, and TEM results, the uranium oxidation state that favors the uranium stability in the melt is in the order U(VI) > U(V) > U(IV).

Plutonium Solubility and Local Structure in Borosilicate Glasses

A reference borosilicate composition (Pu16MC3) developed under a previous DOE/MD project for Pu immobilization was chosen to study plutonium solubility under oxidizing and reducing conditions. The Pu16MC3 glass contains (in mass%) 42.8 SiO_2, 13.2 B_2O_3, 4.1 Al_2O_3, 4.1 Li_2O, 5.1 Na_2O, 1.5 K_2O, 1.0 Cs_2O, 11.3 Gd_2O_3, 2.1 P_2O_5, and 4.7 Fe_2O_3 in which Gd_2O_3 functions as a neutron absorber.

Preliminary results of the plutonium solubility study were reported in Feng et al. (1998). The results are briefly summarized here: under oxidizing conditions, the solubility was less than 10 mass% PuO_2 at 1450°C; plutonium precipitated as PuO_2. Under reducing conditions, the PuO_2 solubility limit was greater than 40 mass%.

Near-edge and XAFS investigations have been completed for these plutonium glasses. The Pu L_{III} near-edge spectra indicate that, in these glasses, plutonium is either Pu(III) or Pu(IV) depending primarily on the oxidation conditions. In these glasses, Pu(IV) dominates when the conditions are oxidizing and Pu(III) when reducing. As shown in Figure 3c, there exists a broad diffraction peak near 30° two-theta that is also seen in a borosilicate glass containing 47 mass% Gd_2O_3 (insert in Figure 3c). For the Gd_2O_3 glass, we have tentatively identified clusters of approximately 5 nm in diameter (see discussion above). Hence, the high solubility of Pu(III) in the borosilicate glass may be related to the formation of Pu(III)-bearing clusters.

With the XAFS of the plutonium in these glasses, in addition to the near-edge information, we are able to discern trends in the local environment surrounding the plutonium. We do need to provide the caveat that the limited order in these glasses results in metrical parameters (coordination number and distances) with significant uncertainty from all but the nearest shells. This is additionally complicated by

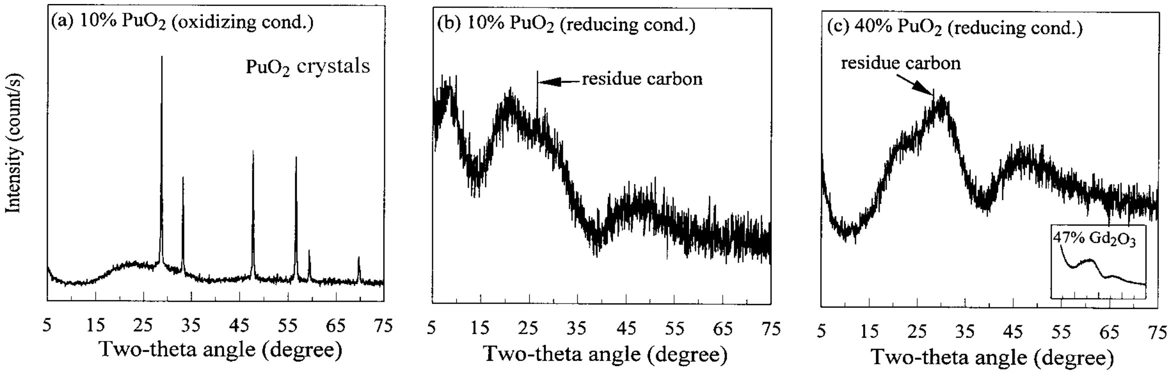

Figure 3. XRD Patterns for the Oxidized (a) and Reduced (b, c) Pu16MC Glasses with Plutonium

the possibility that a significant quantity of the plutonium resides in clusters. We are interpreting the XAFS results with this possibility in mind. The results of the XAFS structural determinations and curve fitting are in the process of being finalized along with the experimental EXAFS results.

Crystalline Waste Forms

This work is directed toward understanding (a) solid solubility limits of plutonium, associated uranium, and the neutron absorbers gadolinium and hafnium, and (b) plutonium and uranium valences in crystalline phases which have had serious consideration for immobilizing waste plutonium and uranium. These phases are zirconolite, $CaZrTi_2O_7$; pyrochlore, $(Ca,An)_2Ti_2O_7$; monazite, $REPO_4$; perovskite, $CaTiO_3$; titanite, $CaTiSiO_5$; apatite, $(Ca,RE,An)_{10}(P,Si)_6O_{26}$; zircon, $ZrSiO_4$; and brannerite, $AnTi_2O_6$, where RE = rare earths and An = actinides.

Uranium in Zirconolite

Sintered $CaZr_{(1-x)}U_xTi_2O_7$ samples were prepared with x varied at 0.1 intervals. From XRD, SEM, and TEM, the zirconolite 2M-4M transition was found to be at x = 0.15 and the pyrochlore/zirconolite boundary near x = 0.65. Synthesis of the end-member $CaUTi_2O_7$ phase is still proving difficult, but hot pressing at 1275°C gave a pyrochlore yield of ~90%, the rest being UO_2. The pyrochlore phase in $CaUTi_2O_7$ samples melted in argon at 1500 and 1550°C was deficient in uranium, having an approximate $Ca_{1.1}U_{0.9}Ti_2O_7$ stoichiometry. Results from x-ray absorption near-edge structure (XANES) measurements at SSRL and diffuse reflectance spectra (DRS) on $CaU_{0.2}Zr_{0.8}Ti_{1.8}Al_{0.2}O_7$ and $CaU_{0.2}Zr_{0.8}Ti_{1.8}Mg_{0.2}O_7$ fired in air and in which the uranium was targeted as U(V) and U(VI), respectively, showed that both the argon- and air-fired samples contained both U(IV) and U(V). The solubility limit of U(IV) on the calcium site was found to be ~0.3 formula units.

Uranium in Perovskite

A perovskite, $Ca_{0.9}U_{0.1}Ti_{0.9}Al_{0.1}O_3$, was fired at 1400°C in argon and H_2/N_2 to target uranium as U(IV) and U(III), respectively. In spite of these attempts, only U(IV) was found in perovskite. Perovskite can incorporate 0.06 formula units of uranium on the calcium site.

Incorporation of Neutron Absorbers and Uranium

Less than 0.02 formula units of hafnium were found to enter the monazite lattice. Brannerite has been found to incorporate ~0.2 formula units of hafnium. Approximately 0.5 formula units of gadolinium can be incorporated in air-fired brannerite, but only 0.1 formula units in argon-fired material. The enhanced gadolinium solubility is consistent with DRS observations indicating U(V) in the gadolinium-doped, but not the undoped material. Titanite was found to incorporate ~0.3 and 0.5 formula units of gadolinium and hafnium, respectively. The incorporation of U(IV) in titanite did not exceed 0.05 formula units.

Summary

We have discussed the results from a variety of microscopic and spectroscopic techniques that we have used in attempts to identify the metal-oxide moiety in the glass. The metastable clusters that appear to form in these glasses form rapidly as the glass cools. Their concentration appears to be dependent on the metal oxide concentration, but our results are inconclusive in this regard. While clusters appear to be metastable, we have no information to suggest that they would alter over a finite time to a more stable form, presumably crystalline in nature. The metastability of these clusters, should they be definitively shown to exist, should be a study that is carried out in some future program.

Several gaps have been filled in our understanding of the solid solubility of plutonium, uranium, and the neutron absorbers hafnium and gadolinium in candidate crystalline waste form phases and, so far, the valences of uranium. This knowledge will be ultimately valuable for repository licensing.

Planned Activities

If clusters exist for metal oxides in glass, it will be one of the major findings for this project. Understanding the nature of these clusters will be the key to the solubility mechanisms for high-valence metal cations such as lanthanide (gadolinium, lanthanum, neodymium) and actinide elements (uranium, plutonium). Electron energy-loss (EELS) and electron energy loss fine structure (ELFS) studies have been started for both plutonium- and gadolinium-doped glasses. We will begin a systematic study of the solubility of Gd_2O_3/HfO_2 mixtures in sodium-alumino-borosilicate glasses to determine the effect of each on the solubility of the other. The solubility of Pu(III) and Pu(IV) will also be investigated. Experiments on selected peralkaline base glasses will be completed. Glasses will continue to be analyzed with EXAFS to determine local glass structures.

To substantiate the U(V) observed in the uranium glasses, a U(V) solid was measured. The uranium XAFS from the glasses is much different than we have seen in several uranates. This leads us to believe that the uranium in the glasses is U(V). Theoretical calculations using FEFF will be performed to model the EXAFS response from U_3O_7 to compare to the uranium glass XAFS while a suitable U(V) material is obtained or prepared for measurement.

The crystalline phases that form as the surrogate oxide become saturated in these glasses will be studied with XRD, SEM, and TEM. The results will help in the understanding of the structure of the crystalline phases and the correlation, if any, to the structure in the glass melt.

The incorporation of hafnium, uranium, and plutonium in the rare-earth apatite with the $Ca_9Gd_{0.33}(Hf, U)_{0.33}(P0_4)_5SiO_4O_2$ stoichiometry and associated whitlockite are currently being studied. The Pu^{3+} and Pu(IV) solubility on the calcium site of sphene and of perovskite will be completed. We will initiate leaching of a selected crystalline phases doped with plutonium, uranium, gadolinium, and hafnium. We will investigate the possible collaboration to determine the uranium oxidation states in glass with DRS.

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