This document was prepared in conjunction with work accomplished under Contract No. DE-AC09-96SR18500 with the U.S. Department of Energy.

EVALUATION OF IMPURITY EXTREMES IN A PLUTONIUM-LOADED BOROSILICATE GLASS

K. M. Fox, C. L. Crawford, J. C. Marra, N. E. Bibler, E. N. Hoffman, and T. B. Edwards
Savannah River National Laboratory
P.O. Box 616, Aiken, SC 29808

ABSTRACT

A vitrification technology utilizing a lanthanide borosilicate (LaBS) glass appears to be a viable option for the disposition of excess weapons-useable plutonium that is not suitable for processing into mixed oxide (MOX) fuel. A significant effort to develop a glass formulation and vitrification process to immobilize plutonium was completed in the mid-1990s. The LaBS glass formulation was found to be capable of immobilizing in excess of 10 wt % Pu and to be tolerant of a range of impurities. To confirm the results of previous testing with surrogate Pu feeds containing impurities, four glass compositions were selected for fabrication with actual plutonium oxide and impurities. The four compositions represented extremes in impurity type and concentration. The homogeneity and durability of these four compositions were measured. The homogeneity of the glasses was evaluated using x-ray diffraction (XRD) and scanning electron microscopy coupled with energy dispersive spectroscopy (SEM/EDS). The XRD results indicated that the glasses were amorphous with no evidence of crystalline species in the glass. The SEM/EDS analyses did show the presence of some undissolved PuO_2 material. The EDS spectra indicated that some of the PuO_2 crystals also contained hafnium oxide. The SEM/EDS analyses showed that there were no heterogeneities in the glass due to the feed impurities. The durability of the glasses was measured using the Product Consistency Test (PCT). The PCT results indicated that the durability of Pu impurity glasses was comparable with Pu glasses without impurities and significantly more durable than the Environmental Assessment (EA) glass used as the benchmark for repository disposition of high-level waste (HLW) glasses.

INTRODUCTION

The United States has identified an excess of up to 50 metric tons (MT) of weapons-useable plutonium. The Department of Energy (DOE) was to construct both a Mixed Oxide Fuel Fabrication Facility (MFFF) and a Plutonium Immobilization Program (PIP) facility to disposition this material. In April 2002, DOE decided not to construct the PIP facility and to solely proceed with the construction of the MFFF facility with a focus only on the disposition of weapons-grade plutonium to meet the non-proliferation agreement between Russia and the United States. This action resulted in up to 13 metric tons of DOE-Office of Environmental Management (DOE-EM) owned, weapons-useable, plutonium-bearing materials having no clear disposition path. The database for the plutonium-bearing feeds with no disposition path was reviewed to identify impurity species and concentration ranges for these impurities. Based on this review, a statistically designed test matrix of glass compositions was formulated to evaluate the ability of the glass to accommodate the impurities. Sixty surrogate LaBS glass compositions (using hafnium oxide as the surrogate for plutonium oxide) were prepared in accordance with the statistically designed test matrix. The heterogeneity (e.g. degree of crystallinity) and durability

(as measured by the Product Consistency Test – Method A (PCT–A) and Toxicity Characteristic Leaching Procedure (TCLP)) of the glasses were used to assess the effects of impurities on glass quality. The results of this testing indicated that the impurities had little impact on the properties of the glasses over the range of concentrations included in the surrogate study [1].

To confirm the results of the surrogate impurity testing, four impurity compositions were selected for testing with plutonium oxide. These compositions represented extremes in both type of impurities and concentrations.

APPROACH

Target Compositions of Selected Glasses

The strategy used in selecting glasses for the impurity variability study is described elsewhere [2]. The target compositions for the surrogate and PuO_2 extreme impurity glasses will be briefly summarized here. Each extreme impurity glass was fabricated using the lanthanide borosilicate Frit X composition [3]. The composition of this frit is given in Table I.

Table I. Composition of LaBS Frit X (in wt% oxides)

Component	wt%
Al_2O_3	10.00
B_2O_3	13.00
Gd_2O_3	13.50
HfO_2	7.00
La_2O_3	19.00
Nd_2O_3	15.00
SiO_2	20.00
SrO	2.50

For the surrogate impurity studies, a series of impurity elements and their concentrations was chosen based on an analysis of the anticipated Pu feeds provided by Moore and Allender [4]. An array of 60 surrogate glass compositions was developed to examine the influence of these impurities on the performance of glasses fabricated with Frit X. The surrogate glasses contained Hf in place of Pu on a mass basis. Based on the results of the surrogate studies and evaluation of the impurity types and levels, four glass compositions were selected for fabrication with PuO_2 for comparison with the surrogate glasses. These glass compositions were selected from the array of surrogate glasses. A letter 'B' was appended to the glass identifiers to distinguish the glasses made with PuO_2 from the surrogates. The glasses selected for fabrication with PuO_2 were as follows:

1. Pu35-03B – this set of impurities represented extreme concentrations of metal ions
2. Pu35-06B – this set of impurities represented extreme concentrations of anions Cl, F and S
3. Pu35-17B – this set of impurities represented extreme concentrations of Cl only (known to have especially low solubility in LaBS glass)
4. Pu04-04B – this set of impurities represented a low concentration of impurities (i.e. extreme concentration of PuO_2).

The target compositions of the four glasses fabricated with PuO_2 are given in Table II.

TableII. Target compositions of the impurity extreme glasses (wt % oxides)

Glass ID	Cl^-	Ta_2O_5	MgO	K_2O	Fe_2O_3	Na_2O	F^-	CaO	Ga_2O_3	NiO	Cr_2O_3	CuO	SO_4
Pu35-03B	0.57	0.18	0.54	0.31	0.14	1.48	0.00	0.77	0.45	0.07	0.64	0.00	0.00
Pu35-06B	0.60	0.10	0.91	0.27	0.97	0.80	0.48	0.29	0.00	0.28	0.22	0.00	0.17
Pu35-17B	1.11	0.55	0.40	0.43	0.00	1.04	0.06	0.08	0.68	0.07	0.31	0.10	0.17
Pu04-04B	0.00	0.00	0.08	0.07	0.08	0.08	0.00	0.08	0.00	0.08	0.09	0.07	0.00
Glass ID	**C**	**PbO**	**SeO_2**	**Cs_2O**	**PuO_2**	**HfO_2**	**Al_2O_3**	**B_2O_3**	**Gd_2O_3**	**La_2O_3**	**Nd_2O_3**	**SiO_2**	**SrO**
Pu35-03B	0.00	0.00	0.00	0.06	8.79	6.02	8.60	11.18	11.61	16.34	12.90	17.20	2.15
Pu35-06B	0.06	0.00	0.00	0.00	8.85	6.02	8.60	11.18	11.61	16.34	12.90	17.20	2.15
Pu35-17B	0.06	0.00	0.00	0.00	8.93	6.02	8.60	11.18	11.61	16.34	12.90	17.20	2.15
Pu04-04B	0.00	0.00	0.00	0.00	9.07	6.02	8.60	11.18	11.61	16.34	12.90	17.20	2.15

Experimental Procedures

Fabrication of the four glasses containing PuO_2 was conducted in the SRNL shielded cells facility. The glasses were batched using reagent grade chemicals and melted for 3 hours at 1450° C. Quenching after each melt was accomplished by partially submerging the crucibles in a pan of room temperature water. The resulting glass was examined visually to identify any heterogeneity (e.g. crystallization in the glass).

Although visual observations for crystallization were performed and documented, representative samples for all quenched and CCC glasses were submitted to SRNL Analytical Development (AD) for X-ray diffraction (XRD) analysis. Samples were run under conditions providing a detection limit of approximately 0.5 vol %. That is, if crystals (or undissolved solids) were present at 0.5 vol % or greater, the diffractometer would not only be capable of detecting the crystals but would also allow a qualitative determination of the type of crystal(s) present. Otherwise, a characteristically high background devoid of crystalline spectral peaks indicates that the glass product is amorphous, suggesting either a completely amorphous product or that the degree of crystallization is below the detection limit. Samples of the glasses were also analyzed by Scanning Electron Microscopy coupled with Energy Dispersive Spectroscopy (SEM/EDS).

The Product Consistency Test (PCT) was performed in triplicate on each glass to assess chemical durability [5]. Also included in the experimental test matrix was the Environmental Assessment (EA) benchmark glass [6] the Approved Reference Material (ARM) glass, and blanks from the sample cleaning batch. Samples were ground, washed, and prepared according to the standard procedure [5]. Normalized release rates for specific elements in the glasses were calculated based on targeted glass compositions.

RESULTS

Visual Observations and XRD Results

No crystallization was visible on the surface or in the bulk of any of the glasses fabricated with PuO_2. Figure 1 is a photograph of these four glasses after being removed from the platinum crucibles in the SRNL shielded cells facility. In addition, all of the glasses were amorphous by XRD. This indicates that the glasses were either free of crystalline material, or that any crystallization was below the XRD detection limit of 0.5 vol %.

Figure 1. Photograph of the four glasses fabricated with PuO_2 in the SRNL shielded cells facility. The glasses are, from left to right, Pu35-03B, Pu35-06B, Pu04-04B and Pu35-17B.

SEM Characterization

Each of the glasses fabricated with PuO_2 was submitted for SEM/EDS analysis. Ground samples were used to provide an increased amount of surface area for analysis. Glass Pu04-04B was generally free of any crystalline phases, as shown in Figure 2. However, some small areas of crystalline material were located, as shown in Figure 3.

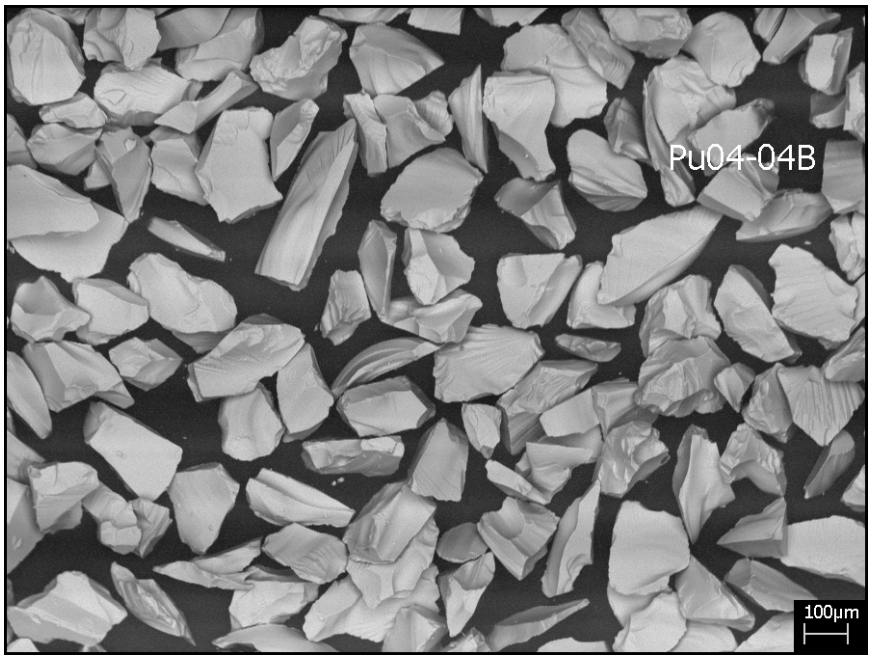

Figure 2. SEM micrograph of glass Pu04-04B. This glass was generally free of any crystalline phases.

Figure 3. Higher magnification SEM micrograph of glass Pu04-04B, showing a small area of crystalline material.

EDS was used to identify the composition of the crystalline phase in Figure 3. A higher magnification image of this region is shown in Figure 4. The areas evaluated with EDS are also indicated in this micrograph. The EDS results for Spot-3 and Spot-4 are shown in Figure 5. The

relative intensities for Pu and Hf are higher in the EDS spectrum for the crystalline phase (Spot-3, Figure 4) than in the glass matrix (Spot-4, Figure 4), indicating that the crystalline phase is composed mainly of these elements.

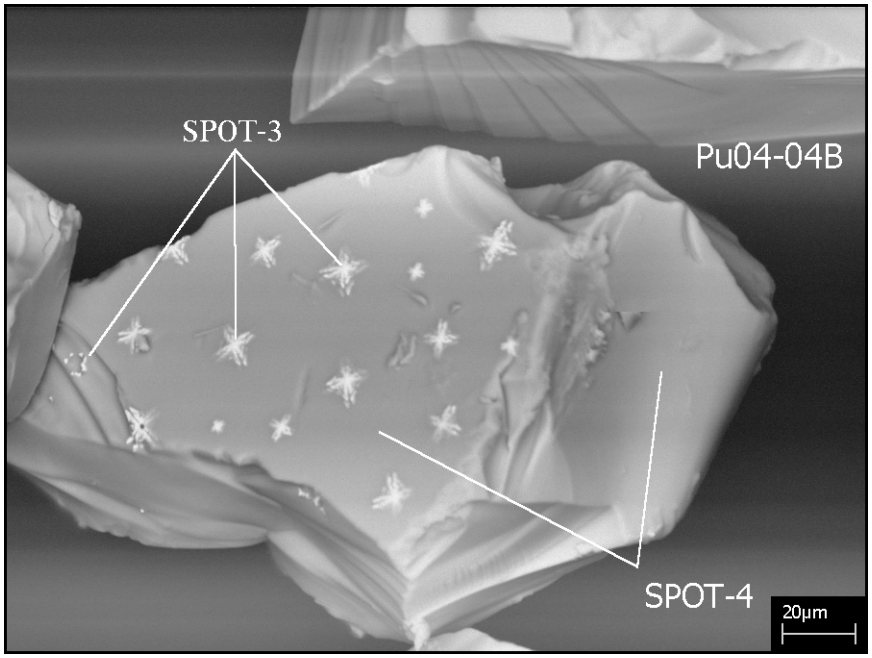

Figure 4. SEM micrograph of the crystalline phase identified in glass Pu04-04B. The marked spots indicate areas where EDS spectra were recorded.

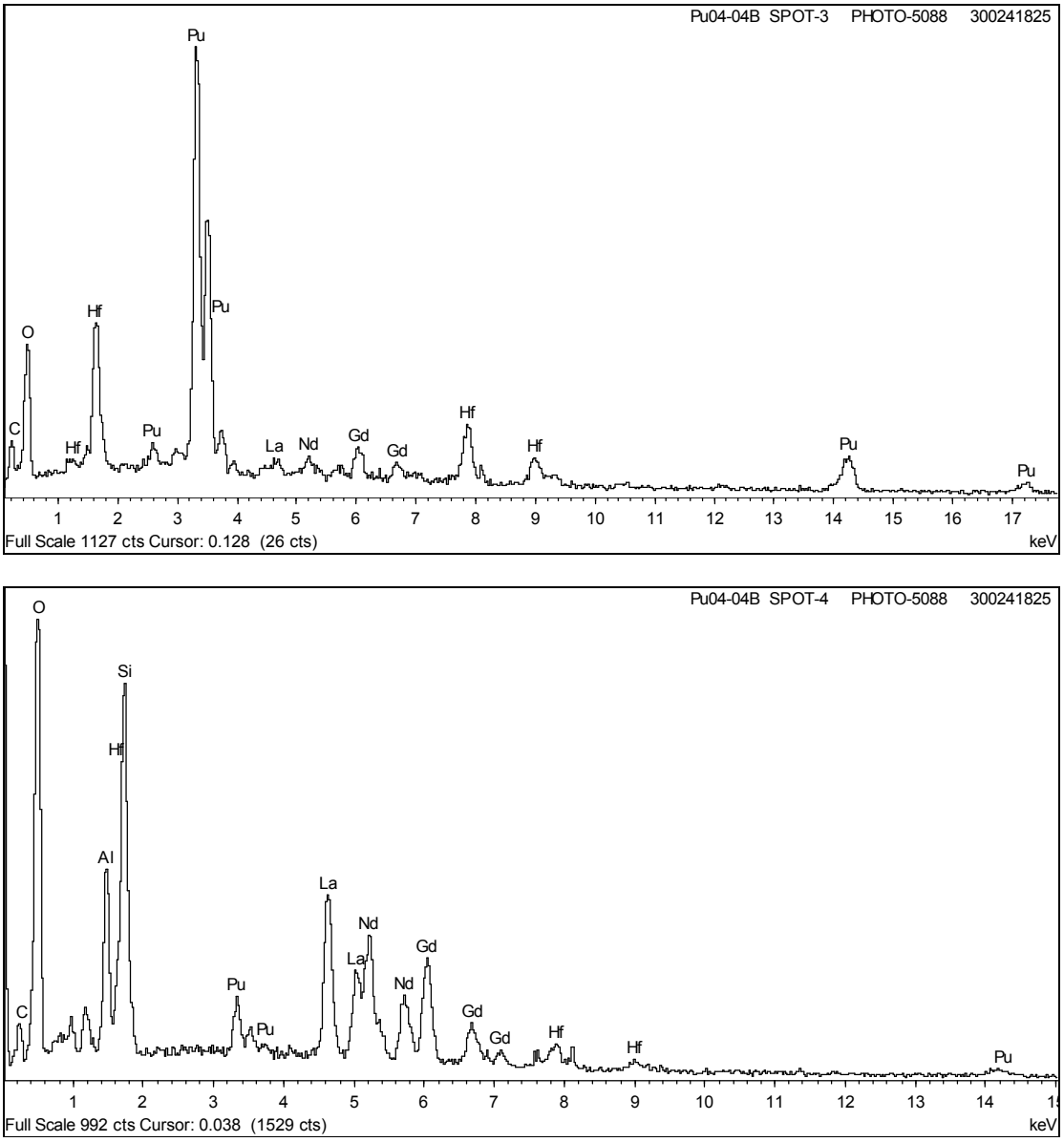

Figure 5. EDS spectra recorded at Spot 3 and Spot-4 in Figure 4.

A Pu-containing crystalline phase with the morphology shown in Figure 4 has been identified in a previous study of Pu-bearing LaBS glasses and may provide an opportunity to intentionally crystallize some of the PuO_2 into a highly insoluble form with Hf acting as an intrinsic neutron absorber [3].

A small amount of crystallization was identified in glass Pu35-03B via SEM. The crystallization appeared to be confined to the faces of individual particles of the glass, as indicated by the arrows in Figure 6.

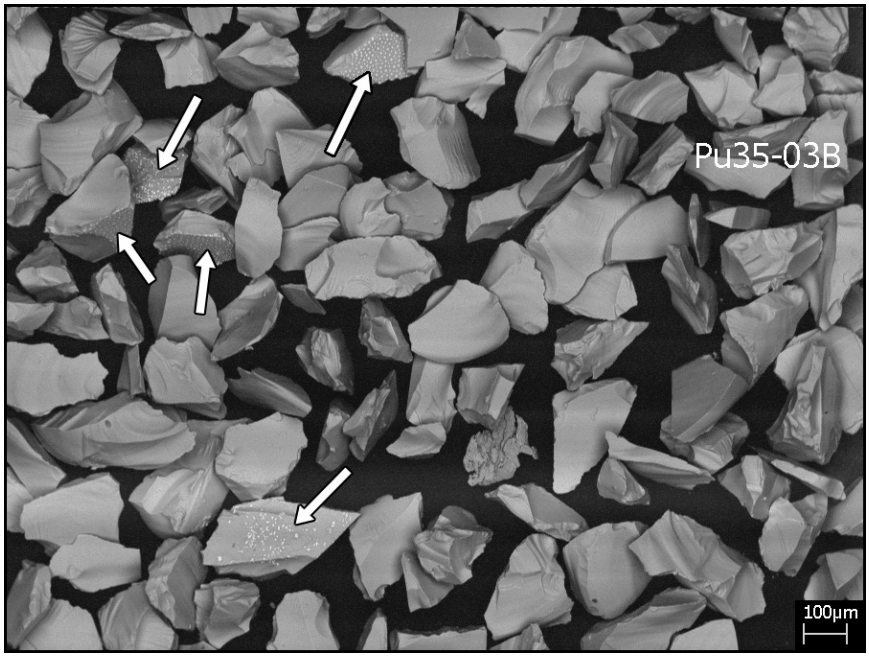

Figure 6. SEM micrograph of glass Pu35-03B. The arrows indicate crystallization on the faces of some of the glass particles.

The crystalline phases in this glass included two morphologies: a simple cube or sphere shape, and a cross shape (as seen in glass Pu04-04B). These morphologies are shown at higher magnification in Figure 7. EDS was used to compare the composition of each of these phases (Spot-1 and Spot-3) with the glass matrix (Spot-2).

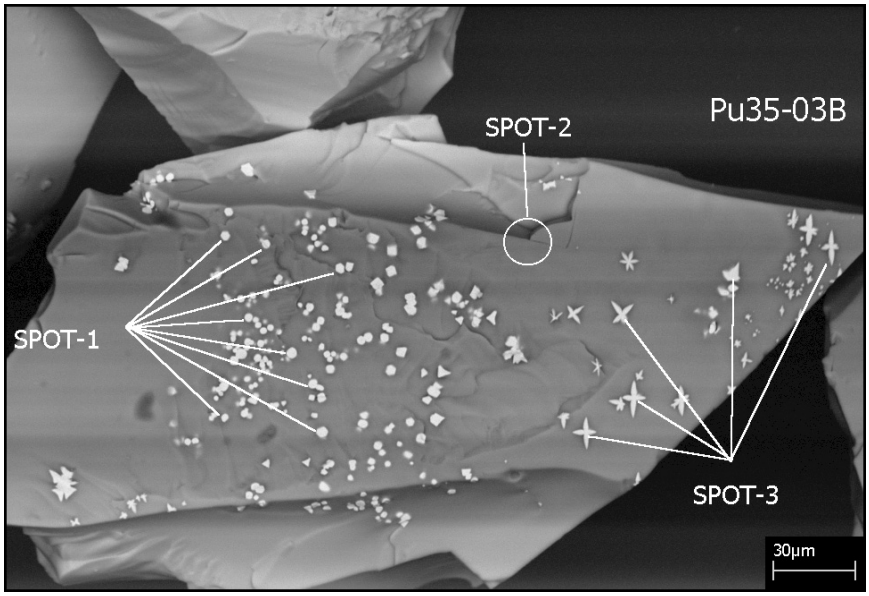

Figure 7. Higher magnification SEM micrograph of the two crystalline phases identified in glass Pu35-03B. Areas analyzed by EDS are indicated.

The EDS spectra are shown in Figure 8. The relative intensities of the EDS peaks for Spot-1 indicate that this phase consists mainly of Pu. The EDS spectrum collected at Spot-3 indicates that this phase consists mainly of Hf and Pu, similar to the crystalline phase in glass Pu04-04B.

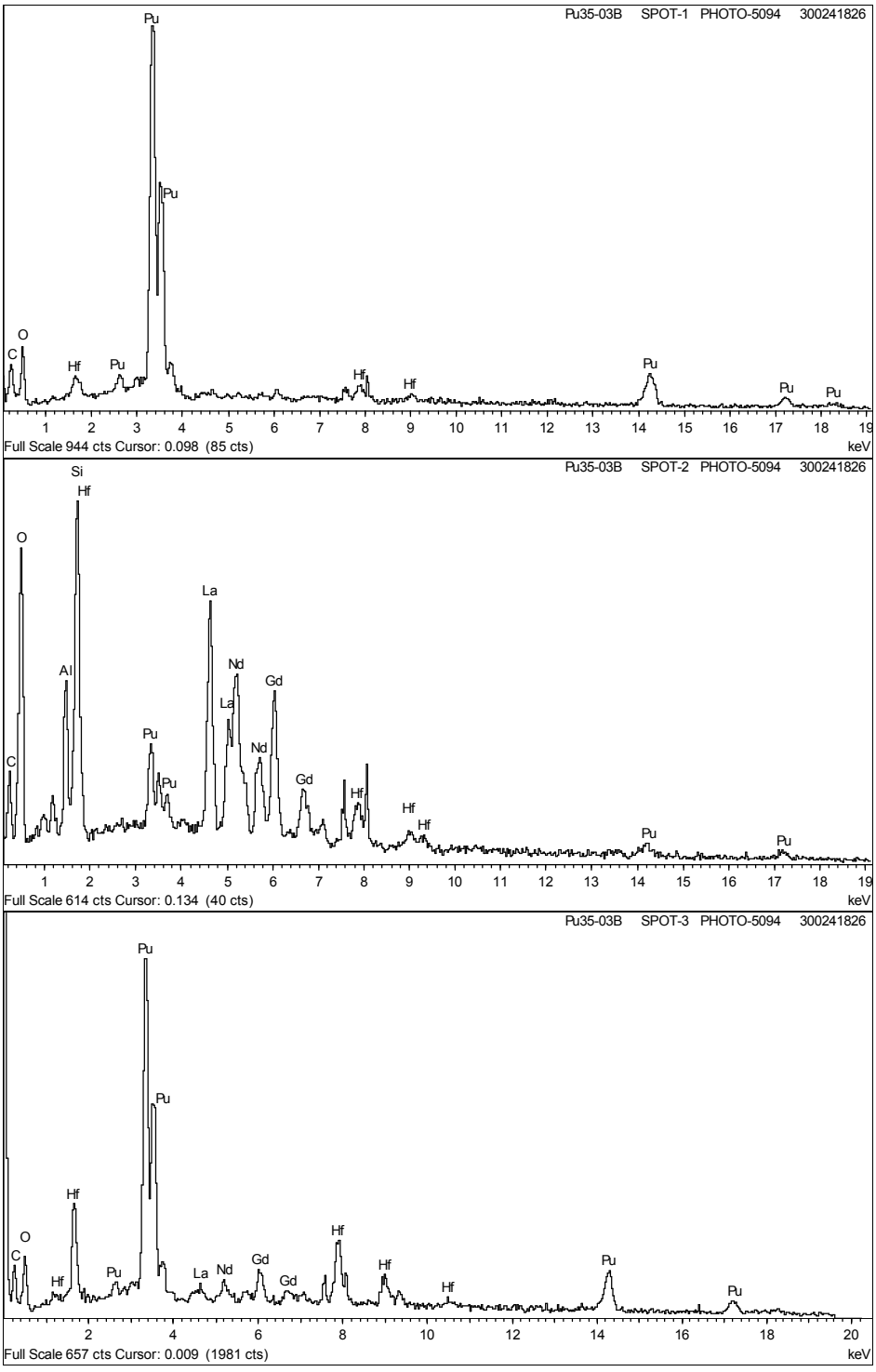

Figure 8. EDS spectra corresponding to the spots identified in Figure 7.

The SEM results for glasses Pu35-06B and Pu35-17B were similar to each other. Both glasses were generally free of crystallization, but a small amount of the cross-shaped phase was identified in each glass. EDS spectra were collected for each glass, and the results were similar to those for the cross-shaped phases identified in glasses Pu04-04B and Pu35-03B.

PCT Results

The four different PuO_2-containing glasses were leach tested in two separate PCT campaigns (PCT #1 and PCT #2) via remote handling in the SRNL shielded cells facility. The PCT Method A was followed using a 10:1 ratio of leachant to glass mass. Each PCT contained two PuO_2-containing glasses, EA glass and ARM glass, all in triplicate. Two blanks were also used. The PCT leachate concentrations for the PuO_2-containing glasses were normalized using the target compositions. The average normalized release values for PCT #1 (Pu04-04B and Pu35-03B) and PCT #2 (Pu35-06B and Pu35-17B) are summarized in Table III. Data for the EA glass and ARM glasses are also shown. Average pH values for the leachates are shown in the last column of Table III. PCT leachates for the PuO_2-containing glasses were analyzed by both ICP-AES (for B, Na and Si) and ICP-MS (for La, Nd, Gd, Hf and Pu). Overall, the normalized release (NL) results for these PuO_2-containing glasses with impurities are similar in magnitude to previous testing performed on PuO_2-containing glasses without any impurities present [7-8]. Comparisons of the EA glass results from the two different PCTs to reference value ranges indicate that NL(B) and NL(Na) average values were slightly under the lower range of EA reference values for PCT-1. The NL(Si) average is within the (average – one standard deviation) of the reference NL(Si). All of the measured EA values are in good agreement with the EA reference values for the PCT-2. Similar comparisons can be made for the measured ARM glass leachate concentrations for PCT-1 and PCT-2 vs. control range values [9]. All of the ARM leachate values determined in PCT-1 and PCT-2 are within the control ranges. It should also be noted that multielement standards were submitted for analysis along with the radioactive leachates. All of these analyzed multielement standard concentrations for B (20 mg/L), Na (81 mg/L) and Si (50 mg/L) agreed with the target values to within ± 4%.

Table III. PCT results for the glasses fabricated with PuO_2.

Glass ID	NL B (g/L)	NL Na (g/L)	NL Si (g/L)	NL La (g/L)	NL Nd (g/L)	NL Gd (g/L)	NL Hf (g/L)	NL Pu (g/L)	pH
Pu04-04B	0.020	<1.587	0.022	0.0003	0.0001	0.0002	< 0.0001	0.0096	7.15±0.4
Pu35-03B	0.014	<0.085	0.017	0.0001	0.0000	0.0000	< 0.0001	0.0061	7.56±0.3
Pu35-06B	0.017	<0.158	0.017	0.0002	0.0001	0.0001	< 0.0001	0.0061	6.91±0.4
Pu35-17B	0.015	<0.122	0.016	0.0002	0.0001	0.0001	< 0.0001	0.0074	657±0.2
EA(PCT-1)	15.171	11.885	3.649						11.49±0.05
EA(PCT-2)	16.943	13.119	3.968						11.64±0.01
EA Ref.	16.695±1.222	13.346±0.902	3.922±0.376						11.85±0.1
ARM Glass*	B (ppm)	Na (ppm)	Si (ppm)						
ARM(PCT-1)	16.8± 0.8	35.9± 1.5	62.2± 1.8						
ARM(PCT-2)	17.7± 0.1	37.5± 0.3	64.2± 0.4						

* Control chart values for ARM glass are B (12.9 – 22.7 ppm), Na (28.9 – 43.6 ppm) and Si (49.0 – 73.4 ppm) [9].

CONCLUSIONS

Four glass compositions were selected from an impurity variability study for preparation with actual PuO_2 and impurities. These compositions represented impurity compositional extremes associated with the anticipated Pu feed stream. The glasses were fabricated and characterized to determine the degree of crystallization that occurred during glass fabrication and to measure the durability of each glass.

Overall, the LaBS glass system appears to be very tolerant of the impurity types and concentrations projected in the Pu waste stream. No crystalline phases or heterogeneities were observed in the glasses via visual examination. XRD scans on the Pu-containing glasses showed no evidence of crystallization. SEM analyses indicated that a Pu-containing crystalline phase with a cross-shaped morphology was identified via SEM in the glasses fabricated with PuO_2. This phase was identified in a previous study of Pu-bearing LaBS glasses and may provide an opportunity to intentionally crystallize some of the PuO_2 into a highly insoluble form with an intrinsic neutron absorber [3]. It is recommended that additional work be conducted to better characterize the influence that this phase has on durability of the glass and methods by which it may be intentionally precipitated. The PCT results for the plutonium-containing LaBS glasses with impurities were similar to previous tests conducted on PuO_2-containing glasses without impurities added. The highest normalized release for boron was 0.02 g/L, which bounded the highest normalized release for Pu of 0.01 g/L.

ACKNOWLEDGEMENTS

The authors would like to thank several individuals at SRNL including: Art Jurgensen, David Missimer, Mike Summer, Curtis Johnson, Jane Howard, Phyllis Burkhalter, Dee Wheeler and Vicki Dukes, all of whom made significant contributions to this study.

REFERENCES

1. K. M. Fox, J. C. Marra, T. B. Edwards, E. N. Hoffman and C. L. Crawford, “Plutonium Feed Impurity Testing in a Lanthanide Borosilicate Glass,” Submitted for publication in **Scientific Basis for Nuclear Waste Management XXXI,** Materials Research Society.

2. K. M. Fox, E. N. Hoffman, T. B. Edwards and J. C. Marra, “Defining a Glass Composition Envelope for an Impurity Variability Study to Support Plutonium Disposition,” U.S. Department of Energy Report WSRC-STI-2007-00368, Revision 0*,* Washington Savannah River Company, Aiken, SC, 2007.

3. J. C. Marra, D. K. Peeler and C. M. Jantzen, “Development of Alternative Glass Formulations for Vitrification of Excess Plutonium,” U.S. Department of Energy Report WSRC-TR-2006-00031, Revision 0, Washington Savannah River Company, Aiken, SC 2006.

4. E. N. Moore and J. S. Allender, "Projected Characteristics of Nominal Feeds to Plutonium Disposition Project," U.S. Department of Energy Report SRNL-OPD-2007-00008, Washington Savannah River Company, Aiken, SC, 2007.

5. ASTM, "Standard Test Methods for Determining Chemical Durability of Nuclear Waste Glasses: The Product Consistency Test (PCT)," **ASTM C-1285***,* 2002.

6. C. M. Jantzen, N. E. Bibler, D. C. Beam, C. L. Crawford and M. A. Pickett, "Characterization of the Defense Waste Processing Facility (DWPF) Environmental Assessment (EA) Glass Standard Reference Material," U.S. Department of Energy Report WSRC-TR-92-346, Revision 1, Westinghouse Savannah River Company, Aiken, SC, 1993.

7. J. C. Marra, C. L. Crawford, and N. E. Bibler, "Glass Fabrication and Product Consistency Testing of Lanthanide Borosilicate Frit B Composition for Plutonium Disposition," U.S. Department of Energy Report WSRC-TR-2006-00033, Revision 0, Washington Savannah River Company, Aiken, SC, 2006.

8. J.C. Marra, C. L. Crawford, and N. E. Bibler, "Glass Fabrication and Product Consistency Testing of Lanthanide Borosilicate Frit X Composition for Plutonium Disposition," U.S. Department of Energy Report WSRC-STI-2006-00318, Revision 0, Washington Savannah River Company, Aiken, SC, 2006.

9. C. M. Jantzen, M. A. Pickett, K. G. Brown, T. B. Edwards, and D. C. Beam, "Process/Product Models for the DWPF: Part 1. Predicting the glass Durability from Composition Using a Thermodynamic Energy Hydration Model (THERMO) (U)," Volume 2: Appendix G, Pages G9 – G11, U.S. Department of Energy Report WSRC-TR-93-672, Rev. 1, 1995.