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Revision 0

DEVELOPMENT OF AN ALTERNATIVE GLASS FORMULATION FOR VITRIFICATION OF EXCESS PLUTONIUM

James C. Marra
David K. Peeler
Carol M. Jantzen

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Official: J. C. Duffy, Manager CS;T
(Name and Title)

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January 2006

Savannah River National Laboratory
Aiken, SC 29808

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REVIEWS AND APPROVALS

AUTHOR(S):

James C. Marra 1/18/06
James C. Marra, Material Science and Technology Date

David Peeler 1/19/06
David K. Peeler, Process Science and Engineering Date

Carol M Jantzen 1/19/06
Carol M. Jantzen, Process Science and Engineering Date

TECHNICAL REVIEWER:

Connie C. Herman 1/18/06
Connie C. Herman, Process Science and Engineering Date

APPROVERS

1/19/06
Natraj C. Iyer, Director, Materials Science and Technology Date

REEdwards 1/19/06
Richard E. Edwards, Manager, Process Science and Engineering Date

1/19/06
Matthew K. Hackney, Nuclear Materials Management Engineering Date

EXECUTIVE SUMMARY

The Department of Energy Office of Environmental Management (DOE/EM) plans to conduct the Plutonium Disposition Project at the Savannah River Site (SRS) to disposition excess weapons-usable plutonium. A plutonium glass waste form is a leading candidate for immobilization of the plutonium for subsequent disposition in a geologic repository. A reference glass composition (Lanthanide Borosilicate ($\underline{La}_2O_3$-$\underline{B}_2O_3$-$\underline{S}iO_2$ (LaBS)) – Frit B) was developed and testing with the LaBS Frit B composition is underway to provide data to support the Yucca Mountain License Application process. The objective of this task was to investigate alternative frit compositions and/or processing conditions that may improve the performance of the reference Frit B – LaBS glass in the repository. The current LaBS Frit B composition was used as the baseline for alternative glass formulation development efforts. A review of the literature and past high actinide concentration glass development efforts was conducted to formulate candidate compositions for testing. Glass science principles were also utilized to determine candidate frit components that may meet task objectives. Additionally, glass processing methods (e.g. slow cooling or induced heat treatment) were investigated as potential means to improve the glass durability and/or minimize fissile material and neutron absorber separation. Based on these analyses, a series of candidate surrogate glasses were fabricated and analyzed. One composition was then selected for fabrication with PuO_2 and subsequently analyzed.

A phase equilibrium approach, developed from the assessment of previous high lanthanide glass formulations, was used to recommend modifications to the SRNL Frit B composition. A specific recommendation to increase Ln_2O_3 [a]content with concurrent reduction of Al_2O_3 and SiO_2 content proved to be successful in improving the melting behavior and component solubility of the glass. This change moved the formulation from a compositional region of potential glass-in-glass phase separation toward a region near a low melting eutectic trough. The resulting LaBS Frit X composition was fabricated and tested.

The chemical durability of the LaBS Frit X glass was shown to be equivalent to the reference Frit B composition as measured by the Product Consistency Test (PCT). The Frit X composition demonstrated improved component solubility in surrogate and plutonium testing. This composition also exhibited improved devitrification behavior that could translate to lower glass processing temperatures and minimize any negative impacts on glass pouring.

Testing with the LaBS Frit X composition also indicated the potential to intentionally precipitate a PuO_2-HfO_2 solid solution phase. This could result in a means to dramatically improve the plutonium leach performance in the repository by the formation of a highly insoluble phase with an inherent neutron absorber. Preliminary testing indicated that glass heat treatment could be used to intentionally form this phase in the glass.

This study identified an alternative LaBS glass composition (Frit X) that should be tested further. Specifically, the suite of performance tests currently being conducted on the reference Frit B composition should be conducted on the Frit X composition to provide the necessary data for repository modeling. The potential to form a PuO_2-HfO_2 phase in the glass should also be further pursued as a potential means to improve waste form performance and criticality control. Additionally, as the feed stream chemistry destined for disposition via vitrification is better defined, a thorough glass formulation variability study should be performed to demonstrate that feed variations can be accommodated in the glass. Finally, this composition should be utilized in melter testing to support project design initiatives.

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[a] Ln_2O_3 refers to rare earth oxides such as La_2O_3, Nd_2O_3, Gd_2O_3, and HfO_2.

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1.0 INTRODUCTION AND BACKGROUND

The Department of Energy Office of Environmental Management (DOE/EM) plans to conduct the Plutonium Disposition Project at the Savannah River Site (SRS) to disposition excess weapons-usable plutonium. Vitrification appears to be a viable option for the disposition of the plutonium. An important part of the vitrification approach is to reduce the attractiveness of the plutonium by fabricating a plutonium glass form and immobilizing the Pu form within the high level waste (HLW) glass prepared in the Defense Waste Processing Facility (DWPF). This requires the Pu Disposition Project schedule to be consistent with EM plans for immobilizing HLW in the DWPF. Therefore, several inputs are needed to provide confidence that the Pu Disposition Project will meet the project schedule. Key inputs are near-term data that will increase confidence that a lanthanide borosilicate (LaBS) glass product is suitable for disposal in the Yucca Mountain Repository.

A workshop was held on April 28, 2005 at Bechtel SAIC Company (BSC) facility in Las Vegas, NV to define the near term data needs. Dissolution rate data and the fate of plutonium oxide and the neutron absorbers during the dissolution process were defined as key data needs. A suite of short-term tests were defined at the workshop to obtain the needed data. The objectives of these short-term tests are to obtain data that can be used to show that the dissolution rate of a LaBS glass is acceptable and to show that the extent of Pu separation from neutron absorbers, as the glass degrades and dissolves, is not likely to lead to criticality concerns. An additional data need was identified regarding the degree of macroscopic cracking that occurs during processing of the Pu glass waste form and subsequent pouring of HLW glass in the DWPF. A final need to evaluate new frit formulations that may increase the durability of the plutonium glass and/or decrease the degree to which neutron absorbers separate from the plutonium during dissolution was identified.

The potential for fissile material and neutron absorber separation is a criticality risk for the repository. The risk can be mitigated by either providing a glass that has a durability that is sufficiently high to preclude criticality even if separation of fissile material from the neutron absorbers occurs (i.e. Pu release rates so low to completely preclude criticality) or ensuring that sufficient neutron absorber is retained with the fissile material during dissolution. Bechtel SAIC Company is currently conducting analyses that will provide guidance concerning the maximum glass dissolution rate and maximum extent of Pu/neutron absorber separation that are acceptable. Testing and analyses are underway with Frit B which may prove to meet repository requirements. However, it was deemed prudent to assess alternative compositions in parallel with these analyses. Past and future test results with the LaBS glass compositions will be evaluated against these requirements. This report summarizes the work completed to date to develop a new frit composition and/or processing strategy to improve the durability of the Pu glass and/or decrease the degree to which neutron absorbers separate from the plutonium during dissolution. Other data needs will be documented elsewhere.

1.1 Previous Actinide Glass Formulation Development

High lanthanide glass compositions were developed commercially in the 1930s for use in optical applications.[1] This family of high lanthanide glasses has been used extensively in nuclear applications for protective purposes since many of the lanthanide elements have large thermal neutron cross-sections.[2] The initial glass composition developed for the vitrification of plutonium was based on these high lanthanide content glasses with the expectation that the ability to accommodate high lanthanide content would translate to the accommodation of plutonium within the glass.[3,4] The ability of high lanthanide content glasses to accommodate plutonium was demonstrated with this composition and the resulting glass was shown to exhibit excellent durability (as defined by the Product Consistency Test (PCT)). A drawback was identified with this composition, however, in that the formulation included listed Resource Conservation and Recovery Act (RCRA) metals namely lead and barium.

In support of the Plutonium Immobilization Program (PIP), plutonium glass formulation development continued with a concerted effort to remove the listed RCRA metals from the formulation yet still maintain high actinide solubility and excellent chemical durability. Efforts were successful in removing the RCRA metals and the initial composition Lanthanide Borosilicate (LaBS) composition was developed.[5] This glass was later denoted as the LaBS Frit A composition. To prove the technical and economic feasibility of dispositioning excess weapons usable materials with the LaBS Frit A composition, it was necessary to demonstrate that PuO_2 feedstock could be readily incorporated into glass in sufficient quantities. The results of these studies showed that PuO_2 solubility could be as high as 13.4 wt % (11.8 wt % elemental Pu) and that these quantities could be incorporated in the glass in less than 4 hours.[6] Incorporation (complete dissolution) could be accomplished in as little as 1 hour with the assistance of agitation and/or using feed with fine particle sizes.

LaBS Frit A employed only gadolinium as a neutron absorber. When it was noted that incorporation of hafnium in the composition would benefit the criticality performance, hafnium replaced zirconium in the frit and the LaBS Frit B formulation was developed.[7] Actinide solubility testing with the Frit B composition was primarily performed with combinations of plutonium and uranium to more accurately reflect the expected excess weapons useable plutonium feed streams. The solubility of combinations of plutonium and uranium was shown to be even higher than for Pu only. For example, a homogeneous glass containing 9 wt % PuO_2 and 6 wt % UO_3 was fabricated for a total actinide loading of 15 wt %.[8] Previous PCT measurements on Frit A and Frit B based glasses have shown normalized boron releases on the order of approximately 0.02 g/L.[9,10] It should be noted that these normalized release rates are better than two orders of magnitude lower as measured by the PCT than the Environmental Assessment (EA) glass that is currently used as the benchmark for disposition of HLW glasses in the repository.[11]

The primary frit compositions used to support previous assessments are shown in Table 1 (on a wt % basis).

Table 1. Previously Developed Plutonium Frit Formulations (wt %).

Oxide	LOFFLER BASED	FRIT A	FRIT B
Al_2O_3	9.0	21.5	21.3
B_2O_3	5.0	11.7	11.6
BaO	2.0	--	--
Gd_2O_3	--	8.6	12.8
HfO_2	--	--	6.6
La_2O_3	18.3	12.4	8.1
Nd_2O_3	32.5	12.8	8.2
PbO	7.9	--	--
Pr_2O_3	3.2		
SiO_2	21.5	29.2	28.9
SrO	--	2.5	2.5
ZrO_2	--	1.3	--

2.0 APPROACH

2.1 Overview

The objective of this task was to investigate alternative frit compositions and/or processing conditions that may improve the performance of the Pu glass in the repository. The current LaBS Frit B composition was used as the baseline for alternative glass formulation development efforts. A review of the literature and past high actinide concentration glass development efforts was conducted to formulate candidate compositions for testing. This included evaluation of previous testing with LaBS Frit A and Frit B compositions. Glass science structural principles were also utilized to determine candidate frit components. Additionally, glass processing methods (e.g. slow cooling or induced heat treatment) were investigated as potential means to improve the glass durability and/or minimize fissile material and neutron absorber separation. Surrogate testing (using HfO_2 as a PuO_2 surrogate) was conducted to evaluate the viability of candidate glass systems prior to radioactive testing. Physical and chemical property measurements were made on the surrogate glasses to assess their suitability. To assess the relative durability of these candidate glass compositions, the Product Consistency Test Method A (PCT-A) was performed.[12] The PCT results were compared with previous Pu LaBS glass PCT results to assess the viability of these alternative compositions. Based on the results of the surrogate testing, a candidate composition was selected for Pu glass fabrication and characterization.

2.2 Rationale for Alternative Glass Compositions

2.2.1 High Lanthanide Content Glass Compositions

The commercial lanthanide (rare earth) borosilicate glass upon which the PuO_2 lanthanide glasses were based was first proposed by Loffler[1,2] for use in technical applications where dichroic glasses were needed or for use as decorative highly colored glasses.[1] The lanthanide glasses are known to accommodate Cs, Y, La-Hf (e.g. the lanthanide elements La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu) and the actinides in relatively high concentrations.[2] Therefore, several LaBS glasses based on the Loffler formulation were investigated by SRNL for stabilization of excess weapons grade PuO_2 as discussed in Section 1.1. The high lanthanide glasses were chosen for investigation rather than conventional borosilicate waste glasses that have inherently low solubilities for PuO_2 because of the ability of the lanthanide glasses to solubilize actinides. Loffler's glass is unique in that it combines lanthanide oxides as fluxes in an aluminosilicate type glass in place of the usual alkali metal oxides.[2] The glasses melt at conventional melting temperatures (≥1350° C) but have an extraordinarily low viscosity. The Loffler glasses typically contain 10-70 wt% of some lanthanide oxides, 9-20 wt% Al_2O_3 and the remainder is SiO_2 (21.5-46 wt %).

The first Loffler glass formulations for PuO_2 stabilization were tested by Ramsey et. al.[13] and were very similar to the Loffler composition given in Table 2. The Ramsey Loffler variants were able to stabilize anywhere from 1.85-17.62 wt% ThO_2 (a simulant for PuO_2). Ce_2O_3 was used in place of the La_2O_3 and Pr_2O_3 in the Loffler formulation although a mixture of three lanthanide oxides was retained during all testing (Table 2). Additional testing substituted a variety of different rare earth elements (always a minimum of three) with little impact on the solubility of ThO_2. This was consistent with the finding of the commercial glass industry that the substitution of various rare earths in the lanthanide borosilicate glasses had little effect on any measured physical properties.[2]

The Loffler and early Ramsey glasses contained hazardous Environmental Protection Agency (EPA) Resource and Recovery Act (RCRA) metal oxides such as PbO and BaO as discussed in Section 1.1. Subsequent formulations by Meaker[5,14] substituted Al_2O_3 and SrO for the RCRA metal oxides PbO and BaO and began to examine what combinations of lanthanide oxides (Gd_2O_3, La_2O_3, and Nd_2O_3) could be optimized with the actinides (ThO_2). The lanthanide Gd was chosen as a lanthanide that is also a neutron absorber needed to alleviate criticality concerns at high PuO_2 concentrations in the glass. Samarium and europium oxides were also investigated. A maximum ThO_2 loading of 25 wt% was achieved with one of the Meaker Al_2O_3/SrO formulations[14] and this became the basis for the development of Frit A (Table 1). Further testing of Frit A glass at Pacific Northwest National Laboratory (PNNL) and Savannah River National Laboratory (SRNL) (Table 2) with PuO_2 revealed that the maximum PuO_2 concentration that could be accommodated in Frit A was 13.4 wt% and a concentration of 9.5 wt% was deemed acceptable for criticality concerns. Frit B partially substituted some HfO_2 (an excellent neutron adsorber) for some La_2O_3 and Nd_2O_3 (Table 2).

The change from the PbO/BaO bearing Loffler glasses to the SrO/Al_2O_3 Frit A glasses caused the total Ln_2O_3 content of the glasses to decrease while the Al_2O_3+SiO_2 content increased (Table 2). The additional modification to Frit B which added HfO_2 in place of Ln_2O_3 caused a further decrease in the total Ln_2O_3 content (Table 2). At concentrations of lanthanide oxides, Ln_2O_3, in the range of 15 wt% the SRNL LaBS glass crystallized to lanthanum silicate phases and amorphous phase separation (APS) known as glass-in-glass phase separation was observed.[14] In addition, the liquidus temperature of some of the LaBS formulations were shown to be too low, i.e.. the glass easily crystallized lanthanum silicates and oxides during pouring.[15] Therefore, a glass formulation approach was needed that could be used to avoid regions of rare-earth silicate formation and regions of APS.

None of the ternary oxide phase relations are known in the Ln_2O_3-B_2O_3-SiO_2 system. However, each of the binary oxide systems which comprise the binary sides of the ternary system are known, e.g. Ln_2O_3-SiO_2 (Figure 1) and Sm_2O_3-SiO_2 (Figure 2), La_2O_3-B_2O_3 (Figure 3), and B_2O_3-SiO_2 (Figure 4). The phase diagrams for all the Ln_2O_3-SiO_2 systems are similar (compare Figure 1 and Figure 2). Ln_2O_3-SiO_2 system has three stoichiometric compounds, 1:1, 2:3 and 1:2 Ln_2O_3: SiO_2. Each Ln_2O_3-SiO_2 system has a region of glass-in-glass phase separation at >1:2 Ln_2O_3: SiO_2 with lower stability temperatures of ~1700° C. Each Ln_2O_3-SiO_2 system has one high temperature congruent melting lanthanide silicate compound at 1:1 Ln_2O_3: SiO_2 and one incongruent melting lanthanide silicate compound at 1:2 Ln_2O_3: SiO_2. Likewise, all the Ln_2O_3-B_2O_3 binary phase diagrams are similar.

In order to discuss the phase relations and regions of low melting eutectics in the Ln_2O_3-B_2O_3-SiO_2 system, the Ln_2O_3-B_2O_3-SiO_2 system will be inferred from the projections of the pertinent binary oxide systems (using La_2O_3-SiO_2 and the B_2O_3-SiO_2 systems as the prime example). In this manner the ternary phase relations regarding crystallization and phase separation can be related to the composition of the fluid melts observed by Loffler and the SRNL LaBS glass research to date.

Since the binary oxide systems given in Figure 1 to Figure 4 are in mole % oxide, the compositions from Table 2 have been converted from oxide wt% to oxide mole%. All of the Ln_2O_3 have been grouped together and the phase equilibria analyzed with SiO_2 as the only glass former and with (SiO_2 + Al_2O_3) grouped with SiO_2 due to their similar structural role as glass formers. For the Loffler glass, this simplification of the glass chemistry (including the contribution of the Al_2O_3) accounts for 89.5 wt% of the glass components. For the SRNL LaBS Pu glass, this simplification (including the contribution of the Al_2O_3) accounts for ~88 wt% of the glass chemistry variation.

Table 2. Comparative Oxide Compositions (Wt%) of Lanthanide/Plutonium Borosilicate Glasses

Oxide	Loffler Glass[b]	Ramsey Loffler ThO_2-1	Ramsey Loffler ThO_2-2	Meaker Loffler ThO_2	LaBS PNNL PuO_2	LaBS Frit A PuO_2	LaBS Frit B PuO_2	LaBS Frit X PuO_2	LaBS Frit B ZrO_2	LaBS Frit B HfO_2	LaBS Frit X HfO_2
Al_2O_3	9.0	9.08	3.58	16.25	19.04	19.46	19.27	9.05	20.35	19.17	9.00
BaO	2.0	2.02	2.14	-	-	-	-	-	-	-	-
B_2O_3	5.0	5.05	7.88	8.85	10.4	10.59	10.50	11.77	11.07	10.44	11.70
Ce_2O_3 (Pr_2O_3)	(3.2)	18.61	-	-	-	-	-	-	-	-	-
Gd_2O_3	-	-	-	17.16	7.61	7.78	11.58	12.22	12.23	11.52	12.15
HfO_2 (frit component)	-	-	-	-	-	-	5.97	6.34	6.23	5.94	6.30
HfO_2 (PuO_2 surrogate)	-	-	-	-	-	-	-	-	-	10.00	10.00
La_2O_3	18.3	0.91	1.21	3.80	11.01	11.22	7.33	17.20	7.70	7.29	17.10
Nd_2O_3	32.5	32.81	34.76	4.05	11.37	11.58	7.42	13.58	7.80	7.38	13.50
PbO	7.9	7.97	8.44	-	-	-	-	-	-	-	-
PuO_2 (Pu_2O_3)	-	-	-	-	11.39	9.50†	9.50	9.50	-	-	-
SiO_2	21.5	21.7	24.36	22.0	25.80	26.43	26.15	18.10	27.52	26.01	18.00
SrO (CaO+ZnO)	-	-	-	1.9	2.22	2.26	2.26	2.26	2.42	2.25	2.25
ThO_2 (PuO_2 surrogate)	-	1.85	17.62	25	11.39	-	-	-	-	-	-
ZrO_2 (frit component)	-	-	-	1	1.15	1.18	-	-	-	-	-
ZrO_2 (PuO_2 surrogate)	-	-	-	-	-	-	-	-	4.56	-	-
Na_2O and Li_2O	-	-	-	-	-	-	-	-	-	-	-
Melt Temp (° C)	1350	1400	1425	1475	1450-1500	1500	1500	1500	1500	1500	1500
Total Ln_2O_3	54.0	52.33	35.97	25.0	29.99	30.58	26.33	43.00	27.73	26.19	42.75
Ln_2O_3+(Th,Zr,Hf)O_2	54.0	54.18	53.59	51.0	45.16	40.08	41.80	58.84	38.52	42.13	59.05
SiO_2+Al_2O_3	30.5	30.78	27.94	38.25	44.84	45.89	45.42	27.15	47.87	45.18	27.00
Reference	[2]	WSRC-NB-93-77, p.9	WSRC-NB-93-77, p.23	WSRC-TR-96-0323	PNNL-11346	WSRC-TR-96-0322	WSRC-RP-97-00902	This report	[15]	This report	This report
SUM	99.4	100	99.99	100.01	99.99	100	99.98	100.02	99.88	100.00	100.00

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[b] This glass also has 0.1 wt% As_2O_5 as a fining agent

† maximum waste loading determined to be 13.4 wt% PuO_2

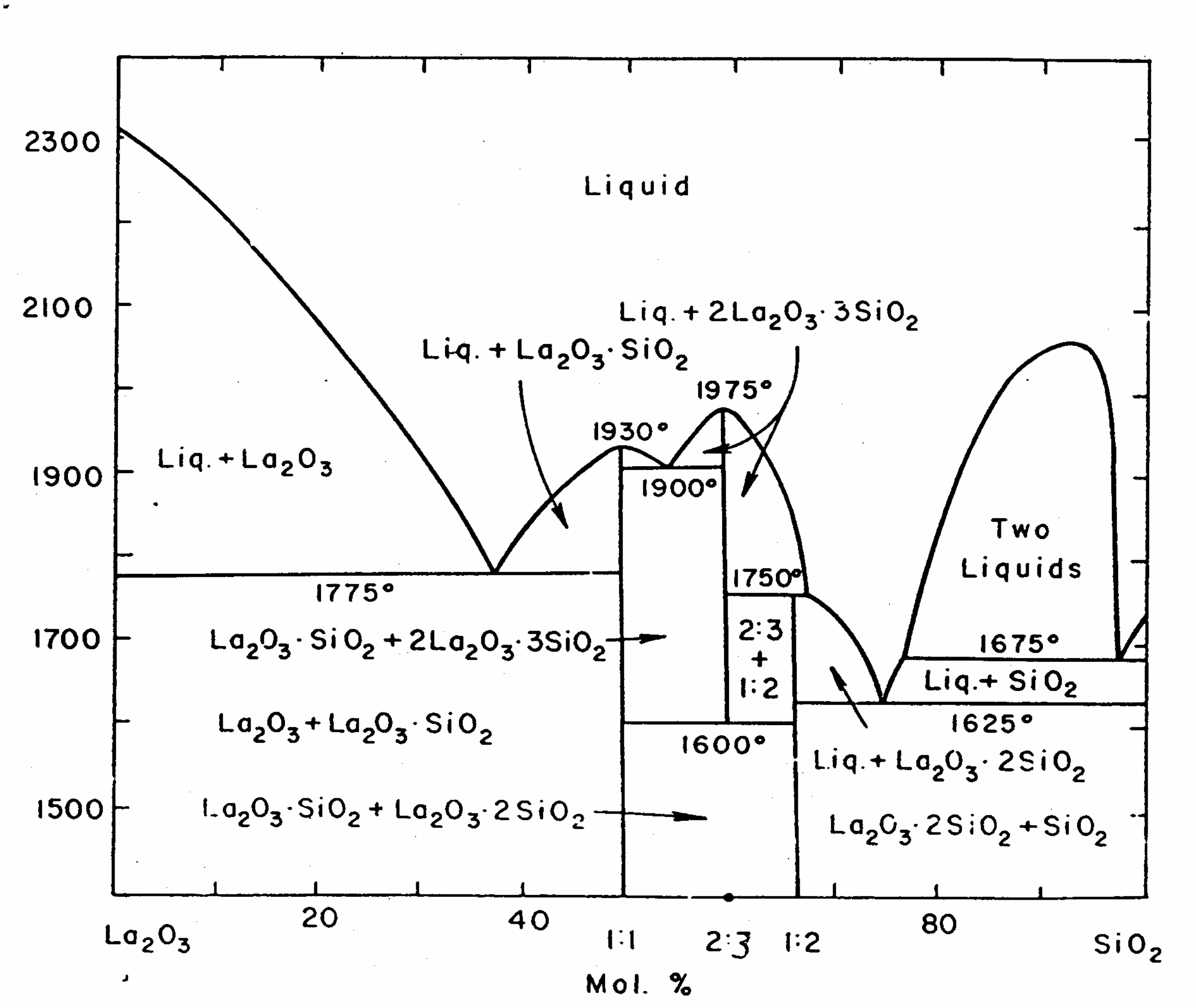


Figure 1. Binary Oxide System La_2O_3-SiO_2 (Figure 2372 from Phase Diagrams for Ceramists, Volume II, Amer. Ceramic Society, Westerville, Ohio, 1969)

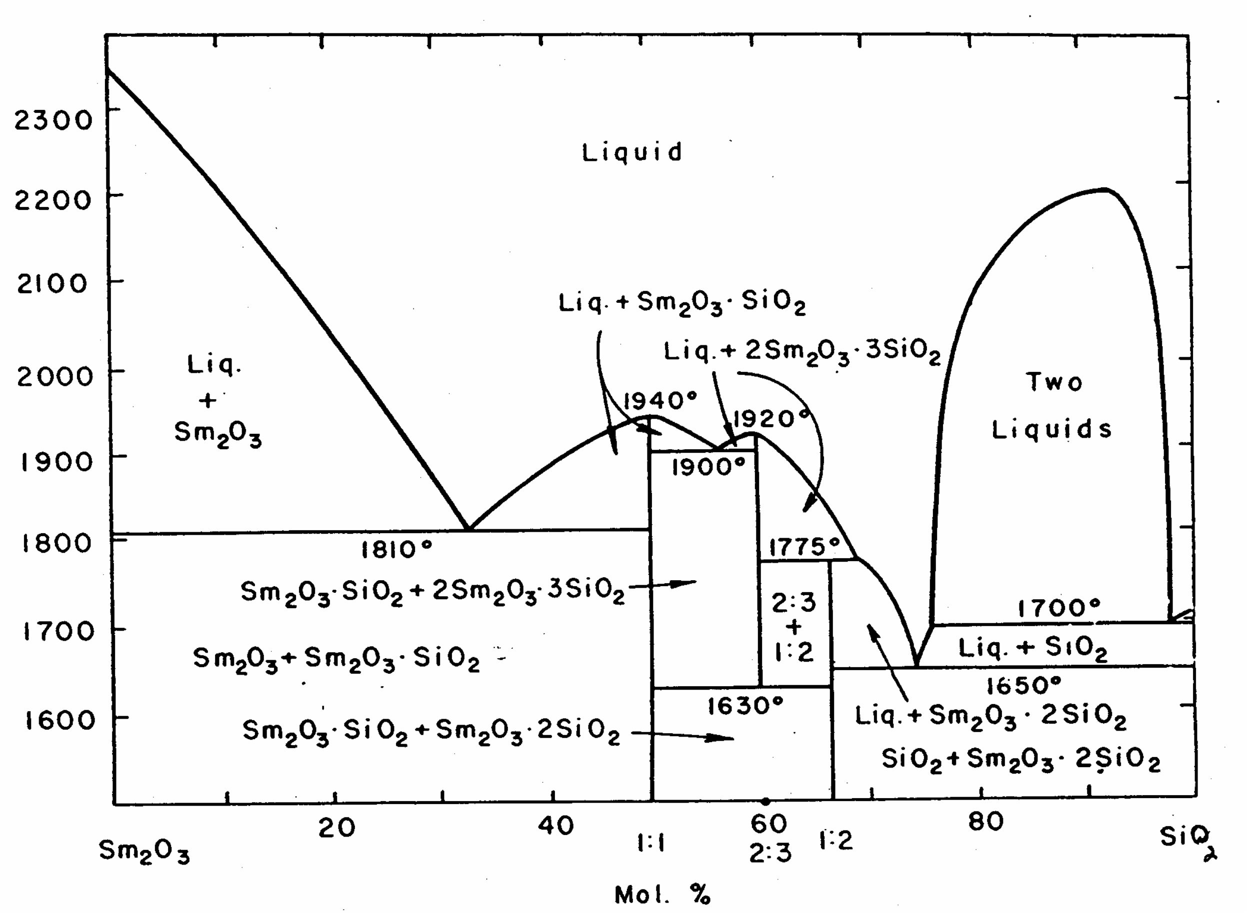


Figure 2. Binary Oxide System Sm_2O_3-SiO_2 (Figure 2386 from Phase Diagrams for Ceramists, Volume II, Amer. Ceramic Society, Westerville, Ohio, 1969)

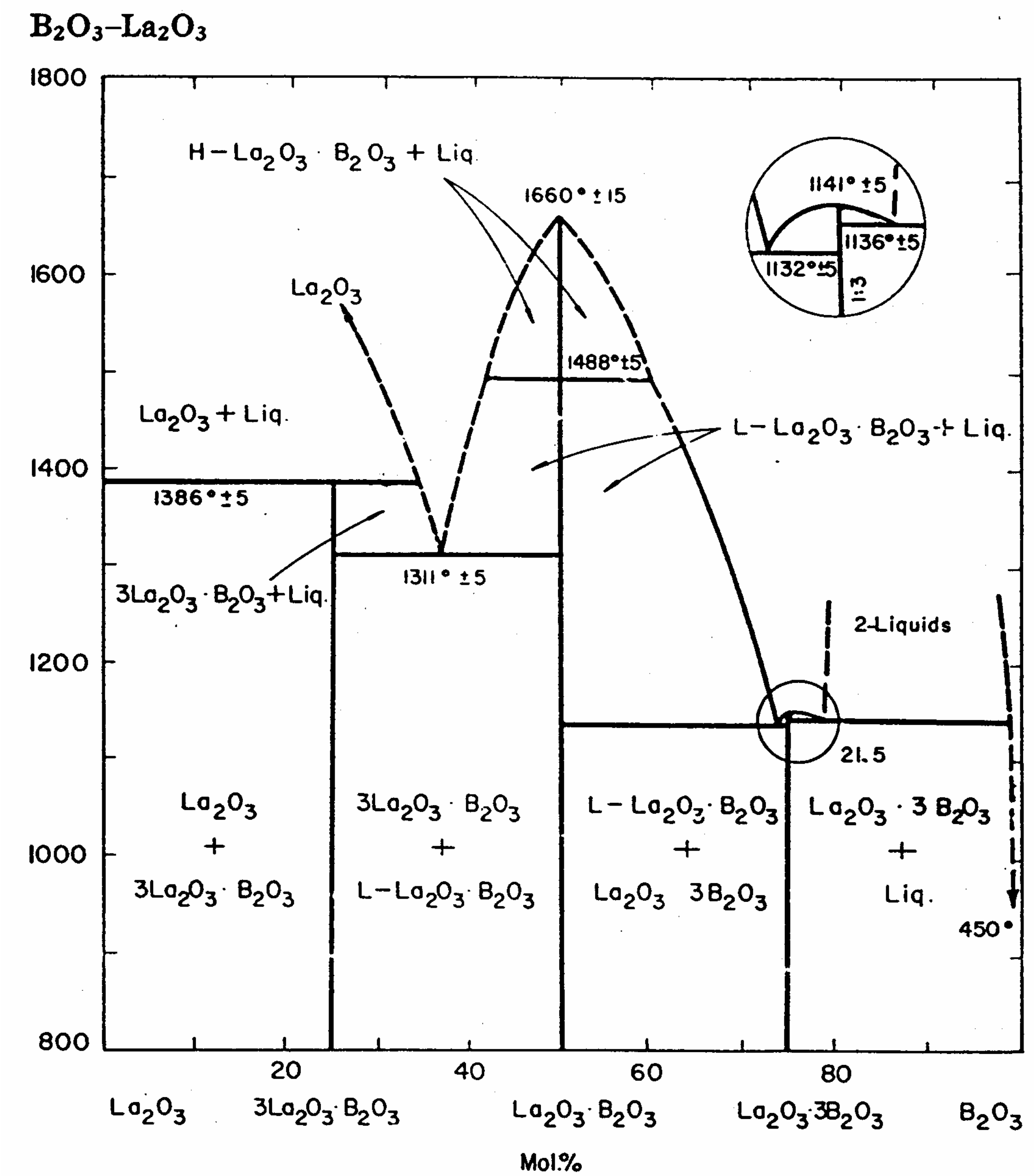


Figure 3. Binary Oxide System La_2O_3-B_2O_3 (Figure 321 from Phase Diagrams for Ceramists, Volume I, Amer. Ceramic Society, Westerville, Ohio, 1964)

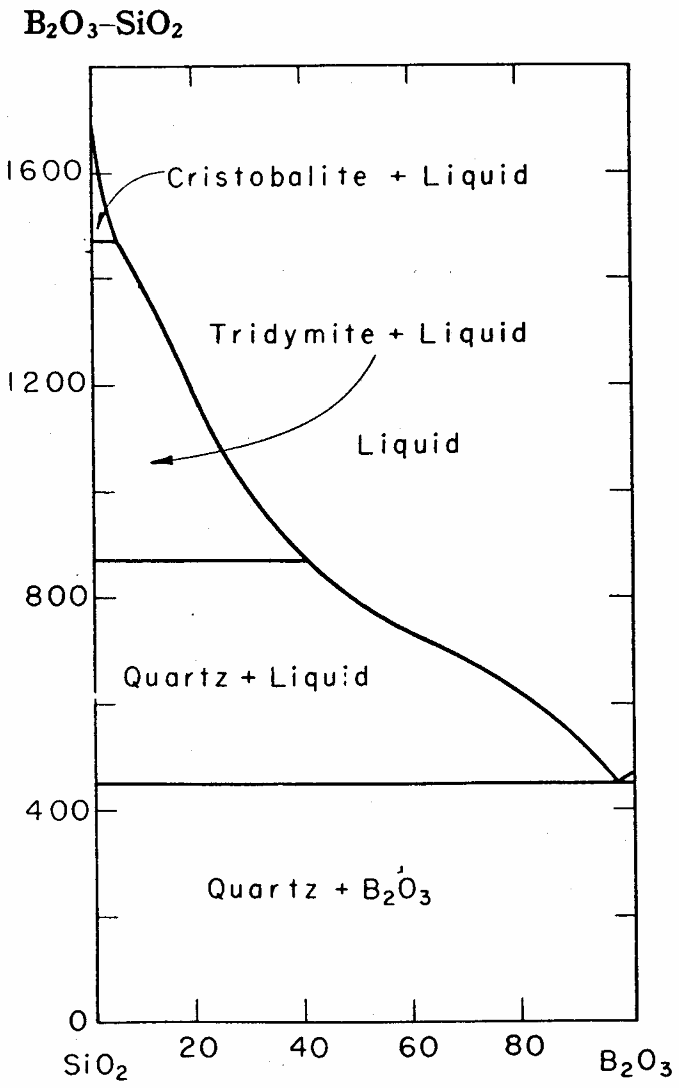
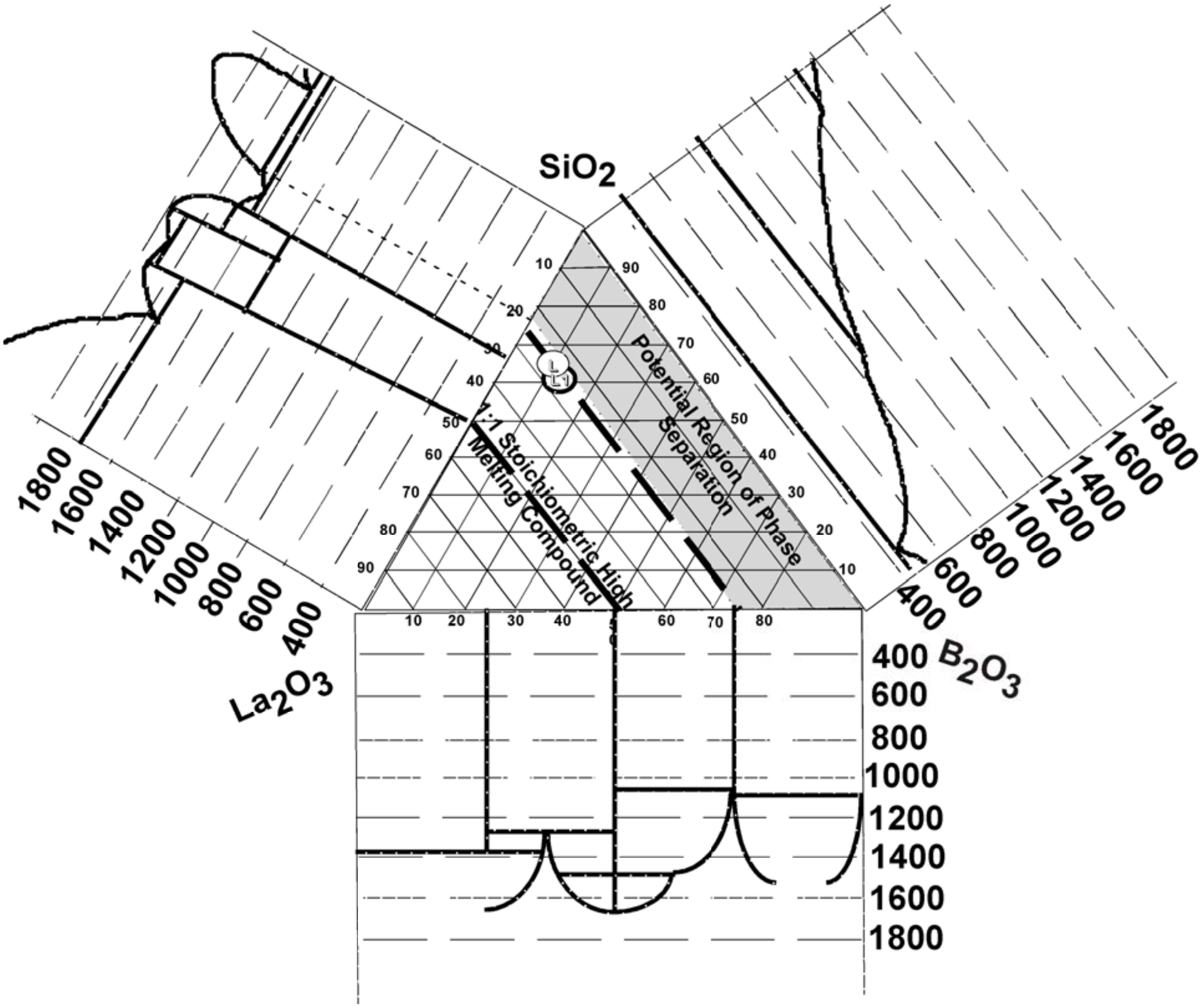


Figure 4. Binary Oxide System B_2O_3-SiO_2 (Figure 2353 from Phase Diagrams for Ceramists, Volume II, Amer. Ceramic Society, Westerville, Ohio, 1969)



Note that the Loffler glass formulation in the Ln_2O_3-B_2O_3-SiO_2 system is indicated in the circle with the letter "L1" and that if the ternary is generalized to include SiO_2+Al_2O_3 at the apex then the Loffler glass formulation in the Ln_2O_3-B_2O_3-(SiO_2+Al_2O_3) system is indicated as "L".

Figure 5. Ternary Oxide System La_2O_3-B_2O_3-SiO_2 generated from the binary oxide systems shown in Figure 1 to Figure 4.

The potential ternary phase relations in the La_2O_3-B_2O_3-(SiO_2+Al_2O_3) system are shown in Figure 5. The 1:1 La_2O_3:SiO_2 stoichiometric compound which melts at 1975° C (Figure 1) more than likely forms a high melting temperature ridge in the ternary system (Figure 5) with the 1:1 La_2O_3: B_2O_3 stoichiometric compound which melts at 1660° C (Figure 3). In the La_2O_3-B_2O_3-(SiO_2+Al_2O3) system (Figure 5) compositions in the proximity of this 1:1 stoichiometric (La_2O_3-B_2O_3):(La_2O_3-SiO_2) ridge will likely have high liquidus temperatures.

The lowest melting temperature glasses can be formed in the La_2O_3-B_2O_3-(SiO_2+Al_2O_3) system (Figure 5) along a trough defined by a line joining the eutectic compositions at 1:3 La_2O_3:SiO_2 (Figure 1 at 22 mole% La_2O_3) and ~1:3 La_2O_3:3B_2O_3 (Figure 3 at 25 mole% La_2O_3). These eutectics melt at temperatures of 1625° C and ~1132-36° C, respectively. Therefore, along the ~1:3 stoichiometric axis shown in Figure 5 compositions higher in B_2O_3 will melt at a lower temperature than compositions enriched in (SiO_2 + Al_2O_3).

At compositions with less molar La_2O_3 than 22-25 mole% on Figure 5, the regions of glass-in-glass (2-liquid) phase separation in Figure 1 and Figure 3 more than likely form a continual dome as indicated by the shaded region in Figure 5. The lower stability temperature of the 2 liquid regions in the La_2O_3-SiO_2 system is ~1700° C while the lower stability temperature of the 2-liquid region in the La_2O_3-B_2O_3 system is 1136° C. This is a region of potential phase separation and should be avoided during glass formulation in this system. Even if a homogeneous glass of this composition can be made by rapid pouring and/or quenching, it will be metastable and tend to phase separate and/or crystallize when subjected to annealing and/or subsequent heat treatment.

The molar composition of the Loffler glass from Table 2 is plotted on Figure 5 as a circle with an “L1” designation. This composition omits any contribution from Al_2O_3. The solid circle with the L designation represents the Loffler glass with Al_2O_3 considered to be structurally equivalent to SiO_2. Both compositions indicate that the high fluidity of the Loffler glass is due to its proximity to the low melting axis in the ternary system that defines the lowest melting eutectics in this system. The presence of PbO in the Loffler glass further served to lower the eutectic melt temperature.

The molar compositions of the SRNL LaBS glasses from Table 2 (Frit A and Frit B at 9.5 wt% PuO_2 loading) are plotted on Figure 6 assuming that Al_2O_3 is structurally equivalent to SiO_2 in these glasses. This is done primarily to demonstrate how the substitution of Al_2O_3 in the LaBS glass formulations in place of PbO[5,14] influenced the LaBS glass homogeneity and solubility. For example, the Loffler glass, the Ramsey ~2 wt% ThO_2 glass, and the Ramsey 17.5 wt% ThO_2 glasses shown on the molar ternary oxide system La_2O_3-B_2O_3-(SiO_2 + Al_2O_3) as stars (*), should all lie in the field of homogeneous glasses as determined in Figure 5 because the glasses were all determined to be homogeneous. Since Loffler states that the lanthanides and the actinides can substitute for each other in the Loffler type glasses, a ternary phase diagram of the (La_2O_3 + XO_2)-B_2O_3-(SiO_2 + Al_2O_3) system (Figure 7), where $XO_2 \equiv PuO_2$, ThO_2, HfO_2 or ZrO_2, was plotted instead. In this combined lanthanide/actinide LaBS system, all three of the homogeneous glasses cited above plot in the region of homogeneous glasses delineated in Figure 5.

Figure 6 and Figure 7 both show that the Meaker base frit (no Ln_2O_3), also indicated by a star (*) in these figures, is in the region of inhomogeneity and indeed, the base frit crystallized $AlBO_4$. As Meaker tried to optimize the LaBS compositions with SrO and Al_2O_3, he continually added more Ln_2O_3 along the line between his base compositions and the Ln_2O_3 +XO_2 apex of Figure 7. Meaker’s data is indicated with open squares (no PuO_2 surrogate), triangles (Pu solubility exceeded), solid circles (glass-in-glass phase separation reported), and solid squares (acceptable glasses). Glasses indicated by open squares in the inhomogeneous region of low Ln_2O_3 +XO_2 content, were indeed phase separated as were some of the solid squares in this region. Meaker’s optimized formulations, Frit A and B at 9.5 wt% PuO_2 are also shown to be in the region of phase separation. Therefore, frit formulations higher Ln_2O_3 appear to be more desirable to avoid phase separation and allow the glass formulations to fall closer to the low melting trough in this system where the Loffler and early SRNL LaBS glass formulations plot.

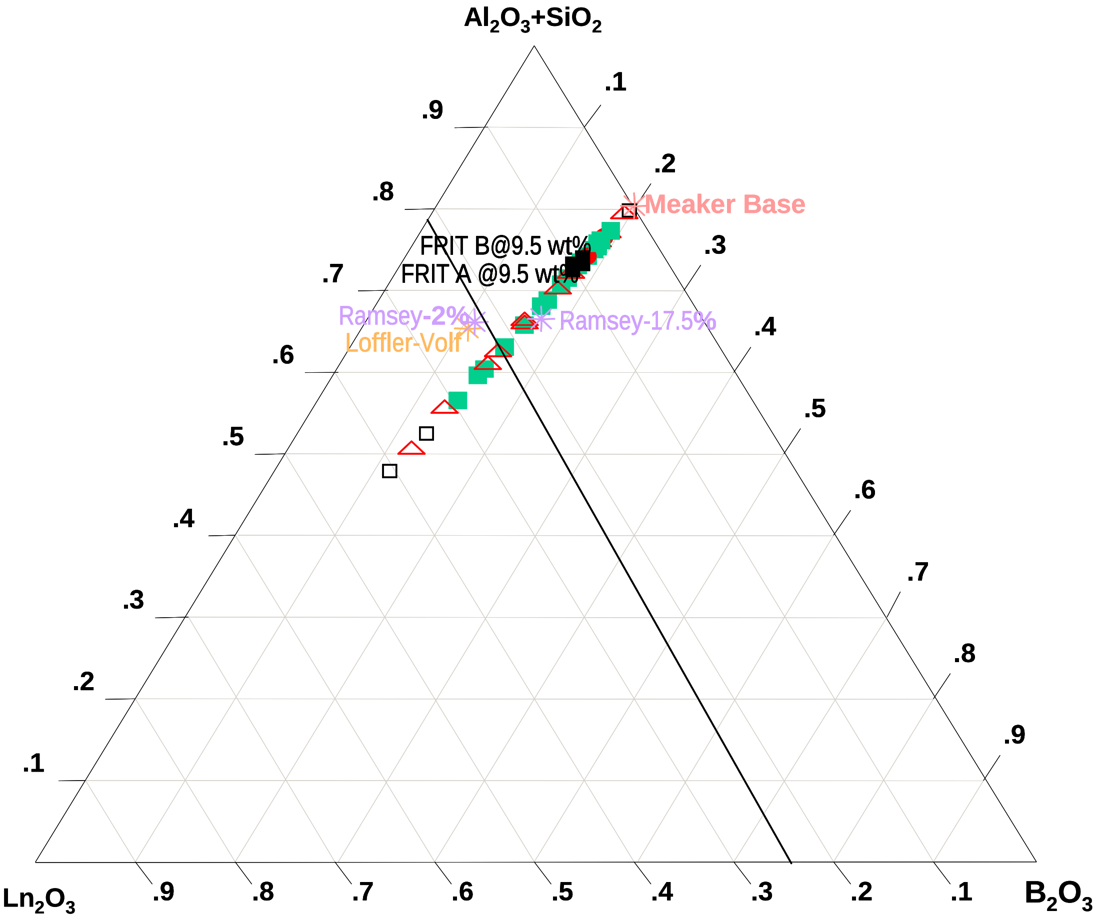
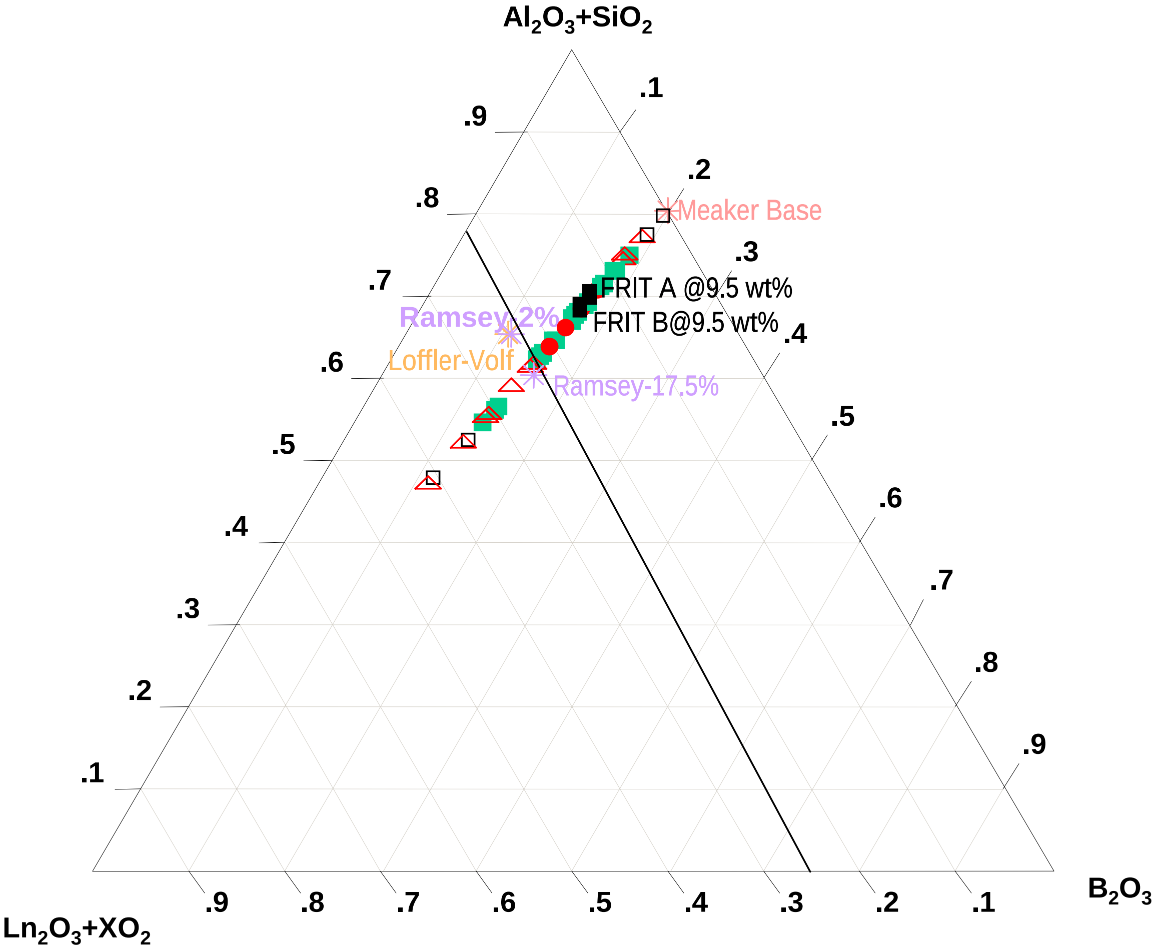


Figure 6. Molar ternary Oxide System La_2O_3-B_2O_3-(SiO_2 + Al_2O_3) with compositions of SRNL LaBS glass formulations tested to date.



XO_2 = PuO_2, ThO_2, HfO_2 or ZrO_2 and HfO_2 and ZrO_2 can be either frit components or PuO_2 surrogates.

Figure 7. Molar ternary Oxide System (La_2O_3 + XO_2) -B_2O_3-(SiO_2 + Al_2O_3) with compositions of SRNL LaBS glass formulations tested to date.

Based on this phase equilibrium approach the following composition modifications to the SRNL Frit A and B LaBS formulations for PuO_2 are recommended:

- Ln_2O_3 needs to be added and Al_2O_3 and SiO_2 content reduced to modify the glass composition so that it is no longer in the range of potential phase separation

- Sufficient Ln_2O_3 should be added and Al_2O_3 and SiO_2 content reduced so that the final glass composition falls on or near the low melting eutectic trough delineated in Figure 5 at ~1:3 stoichiometric axis in the Ln_2O_3-B_2O_3-(SiO_2+Al_2O_3) system

- Compositions lying along the 1:3 stoichiometric axis in the in the Ln_2O_3-B_2O_3-(SiO_2+ Al_2O_3) system (such as the composition shown below) should melt at lower temperatures than the current LaBS formulation and have lower liquidus temperatures:

  50 SiO_2 + Al_2O_3 mole%
  25-30 Ln_2O_3 mole%
  20-25 B_2O_3 mole%

- Mixed Ln_2O_3 should continue to be used instead of just La_2O_3 since the heat of mixing of the rare earth oxides will effectively lower the melt temperature

- If 20-25% B_2O_3 is shown to be ineffective then compositions in the range of the original Loffler glass should be formulated as indicated below

  65 SiO_2 + Al_2O_3 mole%
  27 Ln_2O_3 mole%
  8 B_2O_3 mole%

2.2.2 Additives to Enhance Melting

The current reference Frit B composition requires a melting temperature of nominally 1500° C to ensure dissolution of the constituent frit elements and the plutonium oxide. Glass melting at temperatures in this range is not uncommon in the glass industry; however, melting at elevated temperatures does present a few considerations in processing. The first is volatility from the melt. It is well documented that volatility increases with increasing melt temperature.[2, 16]. The rate of corrosion of melter materials of construction is also directly related to melt temperature.[17, 18] Therefore, means to enhance dissolution and lower the melting temperature are of interest in developing an alternative formulation for plutonium vitrification – consistent or in-line with the recommendations as listed above.

Alkali elements are known to lower melting temperatures and melt viscosities through the formation of non-bridging oxygen ions in the glass.[2, 19] However, the addition of alkali elements in borosilicate glasses has been shown to decrease durability.[20] The impact of iron oxide on durability is typically more neutral in borosilicate glasses yet it can act as a flux to improve melting behavior.[14] Therefore, the addition of iron oxide is a potential candidate for consideration for alternative LaBS glass compositions. It must be noted that iron readily changes oxidation states depending on the reduction/oxidation state of the melt which must be a consideration for compatibility in a Pt/Rh melter system.

2.2.3 Increase in Neutron Absorber

Increasing the neutron absorbers in the glass is also worthy of consideration since the presence of neutron absorbers in the waste form is advantageous for criticality control. Gadolinium oxide and hafnium oxide are present in the baseline Frit B composition and both are known to be excellent neutron absorbers.[21] Compositions with high lanthanide contents could result in increased Gd concentrations. Increasing the hafnium oxide level in the glass may be beneficial because Hf has been shown to have a low aqueous solubility.[22]

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3.0 EXPERIMENTAL PROCEDURES

3.1.1 Simulant Glass Fabrication

Table 3 and Table 4 summarize the baseline frit (Frit B) and 9 initial alternative compositions on a mass% and mol% basis, respectively. As previously discussed, the baseline frit composition (Frit B) has demonstrated relatively high solubility for plutonium and uranium (individually and combination) and exhibited excellent durability (as defined by the PCT). As discussed in Section 2.2, the strategy to support alternative frit development efforts for the actinide bearing glasses were primarily focused on compositional adjustments that could lower the melt temperature (or liquidus temperature) while maintaining or improving glass homogeneity (with respect to Pu solubility) and durability (or performance). Specifically, the compositional adjustments were based on:

- Sufficient Ln_2O_3 should be added and Al_2O_3 and SiO_2 content reduced to avoid potential phase separation and to target the low melting eutectic trough delineated in the Ln_2O_3-B_2O_3 -(SiO_2+Al_2O_3) system.
    - Specifically targeting the 1:3 stoichiometric axis
    - 50 mol% SiO_2 + Al_2O_3, 25 – 30 mol% Ln_2O_3, 20 – 25 mol% B_2O_3

- Mixed Ln_2O_3 should be used instead of La_2O_3 since the heat of mixing of the rare earth oxides will lower the melt temperatures.

    This first two recommendations lead to compositional changes reflected in High Ln_2O_3 #1 – High Ln_2O_3 # 4 which target ~ 52 – 54 mol% SiO_2 + Al_2O_3 (down from ~ 70 mol% in Frit B), 20 – 22 mol% Ln_2O_3 (up from ~12 mol% in Frit B), and B_2O_3 concentrations of approximately 20 – 22 mol% (up from ~ 16 mol% in Frit B). A primary difference between the four alternative glasses is the relative concentrations (or distribution) of Gd_2O_3, HfO_2, La_2O_3, and Nd_2O_3.

- If 20 – 25 mol% B_2O_3 is shown to be effective, then compositions in the range of the original Loffler glass should be formulated.
    - 65 mol% SiO_2 + Al_2O_3, 27 mol% Ln_2O_3, and 8 mol% B_2O_3

    The compositional adjustments made based on this recommendation are expressed through the Loffler #1 and Loffler #2 frit compositions. The mol% SiO_2 + Al_2O_3 in Loffler #1 and Loffler #2 are ~64% and ~67.5%, respectively.

- Fe_2O_3 should be used as an additional flux (as long as it is compatible with the melter materials of construction).

    This recommendation led to the compositional adjustments made in High Fe_2O_3 #1 and High Fe_2O_3 #2 glasses.

- Additional neutron absorber concentrations should be added to improve criticality performance. HfO_2 is especially attractive due to its relatively low aqueous solubility.

This recommendation led to the compositional adjustments made in the High HfO_2 glass.

As indicated, the compositional adjustments were primarily focused on lowering the melt temperature (or liquidus temperature) while maintaining or improving glass homogeneity (with respect to Pu solubility) and durability (or performance). The final compositional adjustment was solely based on increasing neutron absorber content.

Table 3. Target Composition of Baseline and Initial Alternative Frit Compositions (mass%).

Oxide	**Frit B**	**High Ln_2O_3 #1**	**High Ln_2O_3 #2**	**High Ln_2O_3 #3**	**High Ln_2O_3 #4**	**Loffler #1**	**Loffler #2**	**High HfO_2**	**High Fe_2O_3 #1**	**High Fe_2O_3 #2**
Al_2O_3	21.3	12	10	12	10	13	15	21.3	21.3	15
B_2O_3	11.6	13	13	13	13	4.5	5	11.6	11.6	13
Gd_2O_3	12.8	13.5	13.5	19.5	23.5	15	12	9.8	12.8	12.8
HfO_2	6.6	15	6	9	6	15	11.5	9.6	6.6	6
La_2O_3	8.1	12	20	12	10	15	15	8.1	8.1	10
Nd_2O_3	8.2	12	15	12	15	15	14	8.2	8.2	8.2
SiO_2	28.9	20	20	20	20	22	25	28.9	28.9	25
SrO	2.5	2.5	2.5	2.5	2.5	0.5	2.5	2.5	0	0
Fe_2O_3	0	0	0	0	0	0	0	0	2.5	10
Total	100	100	100	100	100	100	100	100	100	100

Table 4. Target Composition of Baseline and Initial Alternative Frit Compositions (mol %).

Oxide	**Frit B**	**High Ln_2O_3 #1**	**High Ln_2O_3 #2**	**High Ln_2O_3 #3**	**High Ln_2O_3 #4**	**Loffler #1**	**Loffler #2**	**High HfO_2**	**High Fe_2O_3 #1**	**High Fe_2O_3 #2**
Al_2O_3	20.96	13.97	12.06	14.17	12.10	16.64	17.63	20.84	21.14	15.79
B_2O_3	16.72	22.17	22.95	22.48	23.04	8.43	8.61	16.62	16.86	20.05
Gd_2O_3	3.54	4.42	4.58	6.48	8.00	5.40	3.97	2.70	3.57	3.79
HfO_2	3.15	8.46	3.50	5.15	3.52	9.30	6.55	4.55	3.17	3.06
La_2O_3	2.49	4.37	7.55	4.43	3.79	6.01	5.52	2.48	2.52	3.30
Nd_2O_3	2.45	4.23	5.48	4.29	5.50	5.82	4.99	2.43	2.47	2.62
SiO_2	48.27	39.52	40.92	40.08	41.08	47.78	49.86	47.98	48.68	44.67
SrO	2.42	2.86	2.97	2.90	2.98	0.63	2.89	2.41	0.00	0.00
Fe_2O_3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.58	6.72
Total	100	100	100	100	100	100	100	100	100	100

Each simulated Pu-glass was prepared from the proper proportions of reagent-grade metal oxides and H_3BO_3 in 100-g batches using HfO_2 as a PuO_2 surrogate. Specifically, each alternative simulated glass targeted 10 mass% HfO_2 (note that this is in addition to the HfO_2 present in the nominal frit composition as listed in Tables 3 and 4). The raw materials were thoroughly mixed and placed into a 95% Platinum/ 5% Rhodium 250-mL crucible. The batch was placed into a high-temperature furnace at the target melt temperature of 1500° C. After an isothermal hold at 1500° C for 2.0 h, the crucible was removed, and the glass was poured onto a clean stainless steel plate and allowed to air cool (quench). The glass pour patty was used as a sampling stock for the various property measurements (i.e., chemical composition, durability, and heat treatments).

3.1.2 Plutonium Glass Fabrication

Based on the results of the surrogate testing, a composition was selected for plutonium glass fabrication. The composition selected was the High Ln_2O_3 #2 Mod (as shown in Tables 3-1 and 3-2). It should be noted that the nomenclature used during the "feasibility" surrogate testing was changed after selecting this frit composition for radioactive testing. The High Ln_2O_3 #2 Mod frit was subsequently renamed Frit X. To facilitate fabrication of the plutonium glass, frit was first prepared in a non-radioactive environment. The frit was prepared by mixing reagent grade chemicals in the proportion for the High Ln_2O_3 #2 Mod (Table 3) scaled to produce a 100 g batch of frit. Oxide chemicals were used for all components except for boron. Boric acid was used to provide the necessary B_2O_3 content in the frit. The frit batch was melted at 1500° C in Pt/Rh crucibles. After nominally two hours at temperature, the crucible was removed from the furnace at temperature and the molten glass poured on a steel plate. The "cullet" pieces were collected for subsequent grinding. The cullet was ground in an automated agate milled and sieved to collect the fraction that was -325 mesh (<45 μm).

After the frit was melted and ground, a sample was analyzed using Inductively Coupled Plasma – Atomic Emission Spectroscopy (ICP-AES) to verify the composition. The sample was prepared by a peroxide fusion (Na_2O_2/NaOH/HCl). The glass sample was prepared in duplicate and was analyzed by ICP-AES to measure the constitutive frit elements.

The plutonium oxide material was obtained from personnel in the Actinide Technology Section of the Savannah River National Laboratory (SRNL). Before using the PuO_2 to fabricate glass, the isotopic content and purity of the material were determined. A sample of the PuO_2 was dissolved in a mixture of 8 M HNO_3/0.05 M KF to facilitate the analyses. Gamma scan and liquid scintillation counting were used to determine the actinide isotopic distribution. To assess for the presence of any impurities, ICP-ES was utilized.

Once the composition of the frit was verified via chemical analysis, the frit was weighed into the appropriate amount to produce 30 g with a target PuO_2 loading of 9.5 wt %. The frit was placed in a plastic bottle for introduction into the SRNL Shielded Cells facility. In the Shielded Cells, the appropriate quantity of PuO_2 was weighed and added to the bottle containing the frit. The bottle was capped and the mixture manually mixed for a few minutes using the rotation afforded by the manipulator arm. The mixture of frit and PuO_2 was placed in a Pt/Rh crucible for melting.[d]

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[d] Previous testing demonstrated that co-grinding the PuO_2 and the frit and manual stirring of the melt enhanced PuO_2 dissolution in the melt. These techniques could not be used in the current fabrication facility.

The Pt/Rh crucible was placed in a high temperature elevator furnace and the furnace was ramped to the melting temperature of 1500° C using a ramp rate of 10° C/minute. The melt was held at temperature for 4 hours and promptly removed from the furnace and quenched in a pan of water. Upon cooling, the glass was manually removed from the crucible by "hammering" the crucible. In this manner nominally 99% of the glass was recovered from the crucible. In an effort to enhance homogenization of the glass, the glass was melted a second time. The glass was melted using the same methodology used for the initial melt.

3.1.3 Glass Characterization

3.1.3.1 Compositional Analysis

To confirm that the "as-fabricated" glasses corresponded to the defined target compositions, a representative sample from each glass was analyzed. The surrogate glass samples were prepared in duplicate using a sodium peroxide/sodium hydroxide (Na_2O_2/NaOH) fusion with a HCl uptake. The peroxide fusion dissolution allows for the analysis of all elemental concentrations of interest (Al, B, Ce, Gd, Hf, La, Nd, Si, Sr, and Fe). The dissolutions were analyzed by ICP-AES.

3.1.3.2 Glass Density

Room temperature density for select simulated Pu glasses was measured by buoyancy (Archimedes method) in water. To support the measurements, an approximate five gram monolithic sample was selected from each pour patty.

3.1.3.3 SEM and XRD Analyses

Scanning Electron Microscopy coupled with Energy Dispersive Spectroscopy (SEM/EDS) and X-ray Diffraction (XRD) were used to assess the homogeneity of both the simulant and Pu containing glasses. Specifically, the analyses were used to examine for the presence of crystalline species and other heterogeneities that may be in the glass. The crystalline species could result from undissolved matter in the glass or phases that crystallized from the glass. The latter was of specific interest for the isothermal heat treatment tests that were conducted (see Section 3.1.5). Analyses were conducted on both shard samples and samples that were ground, sieved and washed according to the protocol used for the PCT. The samples were placed on an aluminum stub to facilitate analysis in the SEM. Crushed glass samples were analyzed by XRD.

3.1.4 Product Consistency Testing

The PCT was performed in triplicate on each simulated Pu-glass to assess chemical durability using technical procedure "Standard Test Methods for Determining Chemical Durability of Nuclear Waste Glasses: The Product Consistency Test (PCT)" (ASTM 2002). Also included in this experimental test matrix was the EA glass,[11] the Approved Reference Material (ARM) glass, and blanks from the sample cleaning batch. Samples were ground, washed, and prepared according to procedure.[11] Fifteen milliliters of Type I American Society for Testing and Materials (ASTM) water were added to ~1.5 g of glass in stainless steel vessels. Due to significant density difference of the simulated Pu glasses and "typical" DWPF glasses, an adjustment to the mass of each glass was made based on the measured density to maintain a "constant" surface area (of glass) to volume (of solution) ratio. Maintaining a constant ratio allows for a direct comparison among the various glasses with respect to durability. Table 5 summarizes the mass of each glass used to support the PCT assessments. The vessels were closed, sealed, and placed in an oven at 90 ± 2° C where the samples were maintained for 7 days. The resulting solutions (once cooled) were sampled (filtered and acidified), labeled, and analyzed. Normalized release rates were calculated based on targeted compositions using the average of the logs of the leachate concentrations.

Table 5. Mass of Glass Used to Support PCT Assessments of Surrogate Glasses.

Glass	Mass of Glass (g)	Volume of H_2O (mL)
EA	1.5	15
Frit B	1.99	15
Fe_2O_3 Based #2	2.12	15
High Ln_2O_3 #2 Mod	2.39	15
High Ln_2O_3 #4 Mod	2.42	15

3.1.5 Isothermal Heat Treatments

During melter testing with the Frit B composition to support the macroscopic surface area determination task, it became evident that the Frit B formulation was susceptible to crystallization at temperatures that could be expected in the Cylindrical Induction Melter (CIM). Therefore, it was necessary to perform testing to benchmark the crystallization behavior of alternative glass compositions to the reference Frit B composition. Moreover, when it was discovered that controlled crystallization may provide the potential to form a plutonium/hafnium phase in the glass, isothermal testing was of additional interest. This latter possibility may be advantageous with respect to minimizing the separation between neutron absorbers and fissile materials.

For simulant glasses, the samples were placed in Pt/Rh crucibles and isothermally heat treated in a high temperature furnace. The furnace was set for the prescribed isothermal temperature and the glass samples were held at temperature for 24 hours. After 24 hours at temperature, the glass was removed from the furnace and allowed to air cool. Due to failure of the high temperature furnace located in the Shielded Cells facility, only limited isothermal heat treatment testing could be performed on the Pu glass. For the Pu glass, a small muffle furnace with a maximum operating temperature of 1200° C was utilized for testing in a radiological hood. Isothermal thermal treatment of the Pu containing glass was conducted on glass shards placed in a Pt/Rh boat. These tests were conducted for 10 hours at the prescribed temperature.[e] After 10 hours at temperature, the furnace door was opened to allow the furnace to cool several hundred degrees before the furnace was shut down to allow the glass to cool in the furnace.

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[e] Since the furnace was being operated near the upper temperature limit, it was felt that testing for 10 hours with frequent monitoring of the furnace was prudent. This duration was deemed adequate for this scoping test.

4.0 RESULTS

4.1 Simulant Glass Visual Observations

Table 6 summarizes the visual observations of the “as-fabricated” simulated Pu glasses (i.e., glasses produced by coupling the nominal frit compositions with 10 mass% HfO_2 as the PuO_2 surrogate). Visual observations were recorded on the pour patty surface as well as the cross section of the pour patty (referred to as the “bulk”). In addition, visual inspection of the glass remaining in the crucible after pouring (referred to as “residual crucible” glass) was made and documented. Although no formal measurement of viscosity was made, visual observations during pouring suggested that the high lanthanide compositions had extremely low viscosities. This may allow for lower melt temperatures.

Prior to discussing the results, a few words regarding the terminology used in Table 6 are warranted. The use of “homogeneous” for visual observations indicates that the sample was classified as a single-phase system (i.e., no evidence of crystallization, undissolved solids, or other inhomogeneities). Glasses characterized by the term “undissolved solids” refers to unreacted or undissolved material (presumably an oxide(s) used as a raw material source that did not go into solution) visually evident in either the pour patty, the residual crucible glass, or both. Other terms used to describe visual characteristics of select glasses include: swirls, coatings, and streaks. These latter descriptors refer to different types of inhomogeneities observed but typically are related to undissolved solids in the glass.

Visual observations of the Frit B glass indicated the presence of undissolved solids in both the pour patty as well as the residual crucible glass. White streaks were also observed in the pour patty which possibly resulted from the undissolved solids being “smeared” as the glass was poured. The undissolved material was HfO_2 – suggesting that the solubility limit had been exceeded under the melt conditions. Based on this observation, a second melt was performed targeting the Frit B glass composition. The primary difference for this second melt was that the glass was batched and melted for 2 hours and poured. After the initial pour, the glass was ground in a tungsten carbide grinder, and remelted at 1500° C for 1 hour to evaluate HfO_2 solubility or homogeneity. Although the pour patty and residual crucible glass were “more homogeneous” than the original Frit B melt, undissolved solids and swirls were still observed (as noted in Table 6).

Table 6. Visual Observations of the "As Fabricated" Baseline and Alternative Pu-Glasses

GLASS ID	VISUAL OBSERVATIONS
Frit B	Undissolved solids in both residual crucible glass and pour patty, "white" streaks in pour patty
Frit B (rebatched/remelted)	Resulting glass still contains some "white" swirls. A little better than the initial Frit B (as noted above) but still undissolved solids and/or swirls present.
High Ln_2O_3 #1	Both residual crucible glass and pour patty contained significant undissolved solids (presumably HfO_2)
High Ln_2O_3 #2	Pour patty and residual crucible glass appeared "single phase" – no undissolved solid noted. Nice "purple" transparent glass.
High Ln_2O_3 #3	Pour patty and residual crucible glass contained undissolved solids. Visually appeared "cleaner" than High Ln_2O_3 #1.
High Ln_2O_3 #4	Pour patty and residual crucible glass appeared "single phase" – no undissolved solid noted. Nice "purple" transparent glass.
Loffler #1	Appeared almost "glass-ceramic"-like. Very inhomogeneous.
Loffler #2	Appeared almost "glass-ceramic"-like. Very inhomogeneous.
High HfO_2	Appeared almost "glass-ceramic"-like. Very inhomogeneous.
High Fe_2O_3 #1	Undissolved solids in pour patty and residual crucible glass (much darker glass due to Fe_2O_3). "White" solids very apparent throughout.
High Fe_2O_3 #2	Glass did not appear to contain undissolved solids. Dark brown/black glass due to Fe_2O_3. The surface of the pour patty was characterized by a "matte" (or crystalline-like) finish – very similar to DWPF type glasses that push toward higher waste loadings yielding devitrification on surface. Cross section of pour patty appeared to be clean or glassy.

Other alternative glasses which resulted in inhomogeneous glass systems included high Ln_2O_3 #1, high Ln_2O_3 #3, both Loffler compositions, the high HfO_2 glass, and the high Fe_2O_3 #1 glass. Based on visual observations, the High Ln_2O_3 #3 was "cleaner" than High Ln_2O_3 #1 however, both contained undissolved solids (presumably HfO_2). Relative to the Frit B glass, the compositional adjustments for these two glasses were "in the right direction" (lower Al_2O_3 and higher mixed Ln_2O_3 concentrations) to lower the melt temperature (or liquidus temperature) while maintaining or improving glass homogeneity (with respect to Pu solubility).

Both Loffler glasses (Loffler #1 and Loffler #2) as well as the high HfO_2 glass were characterized as inhomogeneous as the glasses appeared very opalescent (almost glass-ceramic like) suggesting either amorphous phase separation and/or undissolved solids. The low B_2O_3 content of these glasses coupled with the relatively low Al_2O_3 + SiO_2 concentration appears to a compositional region to be avoided.

The high Fe_2O_3 #1 glass was also characterized by undissolved solids throughout the pour patty as well as the residual crucible glass. The undissolved solids were visually “white” suggesting incomplete dissolution of HfO_2. The high Fe_2O_3 #2 glass did not contain undissolved solids in either the pour patty or the residual crucible glass – suggesting that a significant increase in the Fe_2O_3 content of the frit could result in relative high solubility for HfO_2 (or PuO_2). However, the surface of the pour patty was characterized by a “dull matte” texture. The surface was very similar to simulated high level waste glasses that target relatively high waste loadings resulting in surface devitrification of spinels. The surface coating is not considered to be a technical show-stopper.

Visual observations of the High Ln_2O_3 #2 and High Ln_2O_3 #4 glasses indicated both glasses were very homogeneous with no signs of undissolved solids, swirls, or textured coatings. Both glasses were characterized as a “nice purple, transparent glass.” These two High Ln_2O_3 glasses were based on the compositional direction of adding sufficient Ln_2O_3 while lowering the Al_2O_3 and SiO_2 content to avoid potential phase separation and to target the low melting eutectic trough delineated in the Ln_2O_3-B_2O_3 -(SiO_2+Al_2O_3) system. Given the High Ln_2O_3 #1 and #3 glasses were based on this same theory, the primary difference between the “homogeneous” and “inhomogeneous” glasses was the partitioning of the various rare earths. In general, the High Ln_2O_3 #2 and #4 glasses had slightly lower Al_2O_3 concentrations as well as lower HfO_2 contents than their counterpart high Ln_2O_3 “inhomogeneous” glasses.

Based on these initial melts and visual observations, two additional frit compositions were developed based on the High Ln_2O_3 #2 and High Ln_2O_3 #4 glasses. These frit compositions (referred to as High Ln_2O_3 #2 Mod and High Ln_2O_3 #4 Mod) are listed in Table 7 (both mass% and mol% are shown). The compositional changes to these two “modified” glasses are very minimal as compared to their counterparts. Specifically, the primary difference between the two modified glasses is a 1% increase in the HfO_2 content with the counter reduction coming out of La_2O_3 and Gd_2O_3 for the High Ln_2O_3 #2 Mod and High Ln_2O_3 #4 Mod glasses, respectively. The increase in HfO_2 was driven by the desire to have as much (if not more) contribution of HfO_2 as a neutron absorber as Frit B without compromising product quality or homogeneity.

Table 7. Target Composition of Baseline and Initial Alternative Frit Compositions (mass%)

	High Ln_2O_3 #2 Mod		**High Ln_2O_3 #4 Mod**	
Oxide	Mass %	Mol%	Mass%	Mol%
Al_2O_3	10.00	12.03	10.00	12.07
B_2O_3	13.00	22.91	13.00	22.98
Gd_2O_3	13.50	4.57	22.50	7.64
HfO_2	7.00	4.08	7.00	4.09
La_2O_3	19.00	7.15	10.00	3.78
Nd_2O_3	15.00	5.47	15.00	5.49
SiO_2	20.00	40.83	20.00	40.98
SrO	2.50	2.96	2.50	2.97
Total	100	100	100	100

Visual observations for the two "modified" glasses are summarized in Table 8. Both systems were visually homogeneous with no undissolved solids in the pour patty or residual crucible glass.

Table 8. Visual Observations of High Ln_2O_3 #2 Mod and High Ln_2O_3 #4 Mod

GLASS ID	VISUAL OBSERVATIONS
High Ln_2O_3 #2 Mod	Pour patty and residual crucible glass appeared "single phase" – no undissolved solids. Nice "purple" clear glass.
High Ln_2O_3 #4 Mod	Pour patty and residual crucible glass appeared "single phase" – no undissolved solids. Nice "purple" clear glass.

4.2 Surrogate Glass Characterization

4.2.1 Glass Composition Measurements

In this section, the measured versus targeted compositions of select alternative surrogate Pu glasses are presented and compared. The targeted compositions for these glasses were provided in Tables 3 and 4. The measured elemental concentrations were converted to oxide concentrations by multiplying the values for each element by the gravimetric factor for the corresponding oxide. A sum of oxides was computed for the measured analyses with an acceptance criterion of 95 – 105% sum of oxides used to assess the recovery.

Table 9 summarizes the targeted and measured composition as well as a relative % difference for each of the oxides. Based on a review of the data, the measured compositions agree quite well with the targeted compositions. More specifically, with the exception of the HfO_2 content in the Frit B glass, all of the measurements for each oxide are within ± 10% of the targeted values. This indicates no significant batch errors occurred and/or minimal volatility during the melting process.

With respect to the HfO_2 concentrations for the Frit B glass, the average measured value was ~14.3 wt% in the glass while the targeted concentration was ~15.9 wt% (a ~12% difference). The lower "measured" value can be related to the presence of undissolved solids visually apparent in both the glass pour patty and the residual crucible glass (see Section 4.2.3 for SEM analysis supporting the presence of HfO_2). A closer review of the HfO_2 values for the alternative glasses shows that the measured values are within ±5% of the targeted values. This agrees well with visual observations of homogeneity (i.e., undissolved solids were not visually noted) and suggests that the strategic compositional changes may maintain relatively high actinide solubility.

Table 9. Compositional Analysis of Select Alternative Surrogate Glasses (mass %)

	Al_2O_3	B_2O_3	Fe_2O_3	Gd_2O_3	HfO_2	La_2O_3	Nd_2O_3	SiO_2	SrO	Total
Frit B (A)	19.28	10.53	-	11.18	14.28	7.11	7.21	26.32	2.09	97.99
Frit B (B)	19.28	10.27	-	11.05	14.28	7.04	7.10	25.89	2.09	97.01
Average	19.28	10.40	-	11.11	14.28	7.08	7.15	26.11	2.09	97.50
Target	19.17	10.44	-	11.52	15.94	7.29	7.38	26.01	2.25	100.00
% Relative Difference	0.56	-0.38	-	-3.65	-11.64	-2.99	-3.15	0.38	-7.73	
High Ln_2O_3 #2 (A)	9.53	11.82	-	12.31	14.75	17.67	12.75	18.28	2.12	99.24
High Ln_2O_3 #2 (B)	9.54	11.95	-	12.31	14.87	17.55	12.75	18.58	2.14	99.71
Average	9.54	11.88	-	12.31	14.81	17.61	12.75	18.43	2.13	99.48
Target	9.00	11.70	-	12.15	15.40	18.00	13.50	18.00	2.25	100.00
% Relative Difference	5.61	1.53	-	1.26	-3.99	-2.22	-5.86	2.31	-5.64	
High Ln_2O_3 #4 (A)	9.60	12.20	-	21.28	14.99	8.93	12.40	18.17	2.18	99.82
High Ln_2O_3 #4 (B)	9.58	12.04	-	21.16	15.10	8.93	12.17	18.13	2.24	99.43
Average	9.59	12.12	-	21.22	15.05	8.93	12.29	18.15	2.21	99.63
Target	9.00	11.70	-	21.15	15.40	9.00	13.50	18.00	2.25	
% Relative Difference	6.17	3.49	-	0.32	-2.36	-0.82	-9.89	0.81	-1.69	
Fe_2O_3 based #2 (A)	14.02	11.59	8.95	11.85	14.75	9.11	7.29	22.26	-	100.28
Fe_2O_3 based #2 (B)	13.99	11.50	8.92	11.85	14.63	9.08	7.29	22.26	-	99.97
Average	14.00	11.54	8.94	11.85	14.69	9.10	7.29	22.26	-	100.13
Target	13.50	11.70	9.00	11.52	15.40	9.00	7.38	22.50	-	100.00
% Relative Difference	3.61	-1.35	-0.70	2.74	-4.83	1.06	-1.25	-1.10	-	
High Ln_2O_3 #2 Mod (A)	9.54	11.85	-	12.08	15.93	17.08	13.10	17.95	2.22	99.87
High Ln_2O_3 #2 Mod (B)	9.54	11.95	-	12.31	16.17	17.20	13.46	18.08	2.23	101.04
Average	9.54	11.90	-	12.19	16.05	17.14	13.28	18.02	2.22	100.46
Target	9.00	11.70	-	12.15	16.30	17.10	13.50	18.00	2.25	100.00
% Relative Difference	5.70	1.66	-	0.33	-1.57	0.24	-1.66	0.10	-1.16	
High Ln_2O_3 #4 Mod (A)	9.53	11.85	-	20.24	15.93	8.99	13.34	18.19	2.17	100.26
High Ln_2O_3 #4 Mod (B)	9.51	11.88	-	20.24	16.05	9.03	13.22	17.98	2.21	100.14
Average	9.52	11.87	-	20.24	15.99	9.01	13.28	18.08	2.19	100.20
Target	9.00	11.70	-	20.25	16.30	9.00	13.50	18.00	2.25	100.00
% Relative Difference	5.42	1.40	-	-0.05	-1.95	0.10	-1.66	0.46	-2.79	

4.2.2 Glass Density

Table 10 summarizes the density measurements (in g/cm^3) based on the Archimedes's Method (buoyancy) for select alternative Pu surrogate glasses. Also shown in Table 10 is the density range of a "typical" high level waste (HLW) glass for comparison. As anticipated, the high lanthanide based glasses have higher densities which resulted in the mass adjustment used during the PCT (durability) assessment.

Table 10. Density Measurements for the Alternative Pu Glasses

Glass	Density (g/cm^3)
Frit B	3.58
High Ln_2O_3 #2	4.28
High Ln_2O_3 #4	4.31
Fe_2O_3 Based #2	3.81
High Ln_2O_3 #2 Mod	4.31
High Ln_2O_3 #4 Mod	4.35
"Typical" HLW Glass	2.5 – 2.7

4.2.3 SEM and XRD Analyses

A sample of the surrogate Frit B glass (HfO_2 surrogate for PuO_2) was submitted for SEM analysis to further investigate the visual observations regarding undissolved or crystalline material in the glass. The analysis showed copious quantities of HfO_2 crystals in the glass (Figure 8). The presence of the undissolved HfO_2 provided an early indication of the potential solubility limitations of Frit B with respect to +4 valence elements (further insight was obtained shortly later in Cylindrical Induction Melter (CIM) testing with the Frit B composition – see Section 4.6).

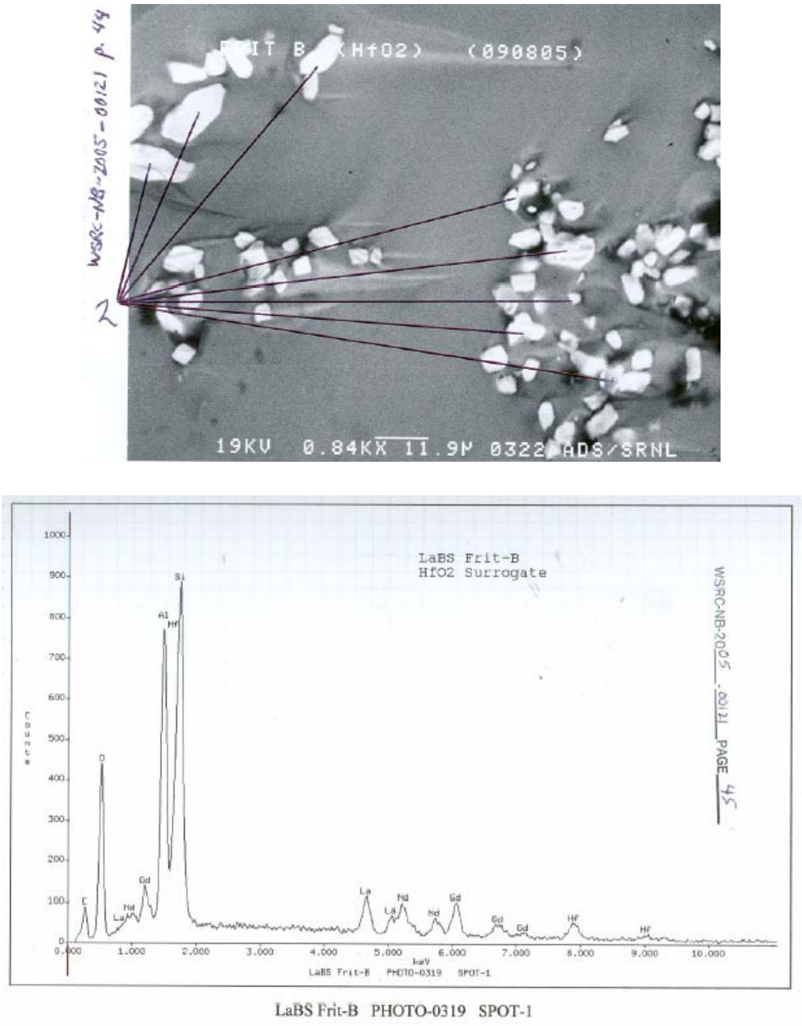


Figure 8. SEM micrograph and corresponding EDS spectrum for surrogate Frit B glass.

A sample of surrogate High Ln_2O_3 #2 Mod glass was also submitted for SEM analysis. The results indicated that the glass was essentially homogeneous with only a few areas where “clusters” of undissolved HfO_2 were observed (Figure 9). A sample of High Ln_2O_3 #2 Mod glass was also submitted for XRD analysis. Samples were run under conditions allowing 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 measure (i.e., determine the type of crystal[s] present). Otherwise, a characteristically high background devoid of crystalline spectral lines indicated that the glass product was amorphous (suggesting either a completely amorphous product or that the degree of crystallization was below the detection limit). Based on these conditions, the XRD scan of the High Ln_2O_3 #2 Mod glass indicated that the glass was amorphous (Figure 10).

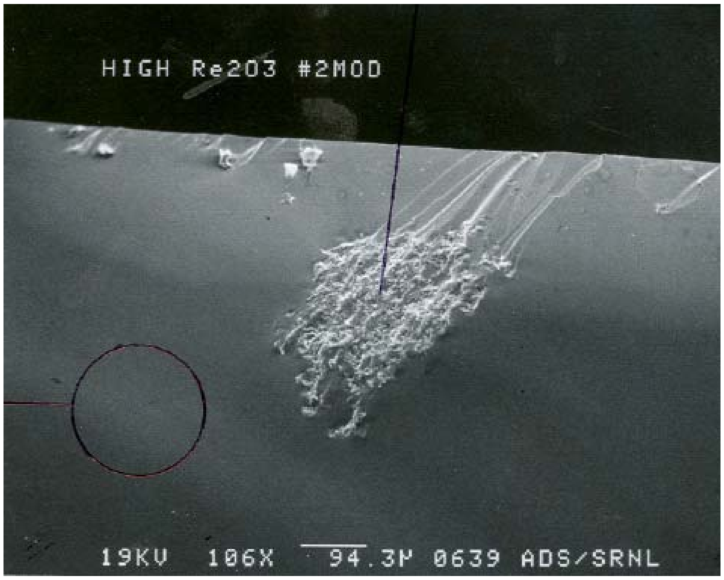


Figure 9. SEM micrograph and corresponding EDS spectrum for surrogate High Ln_2O_3 #2 Mod glass.

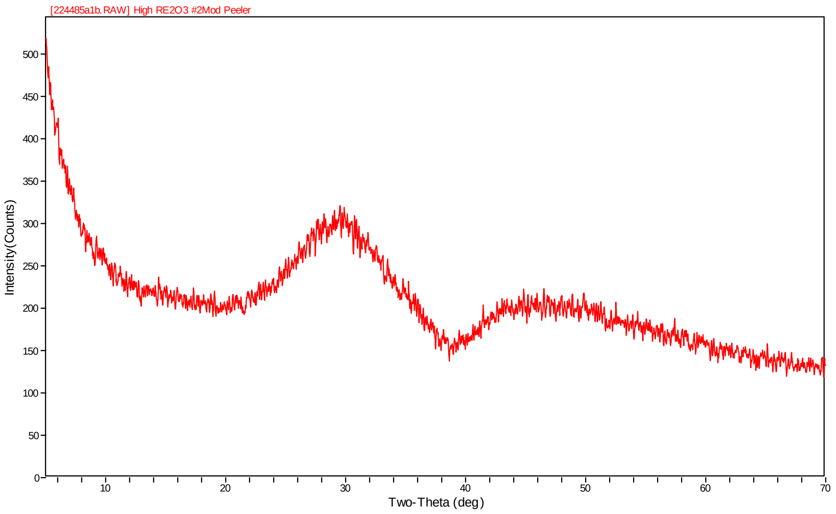


Figure 10. XRD scan for surrogate High Ln_2O_3 #2 Mod glass.

4.3 Surrogate Glass PCT Results

Table 11 summarizes the normalized releases for B and Si (NL [B] and NL [Si], respectively) for select simulated alternative. It should be noted that Li and Na are not reported in Table 11 given the alternative Pu surrogate glasses do not contain these elements. In addition to the normalized releases, the average pH (of the triplicate PCTs) values are reported. The normalized releases and pH values for the Environmental Assessment (EA) glass are those reported by Jantzen et al.[11].

As seen in Table 11, the durabilities for the alternative Pu surrogate glasses are much better than those of EA (this is indicated for a glass by its normalized leachate being smaller than that of EA). The NL [B]s for all of the surrogate glasses are ~ 0.02 g/L with very little if any differentiation (with respect to PCT releases). In terms of "acceptability", all simulated glasses are very acceptable glasses with respect to durability as defined by PCT. The measured normalized releases are consistent with previous assessments for the Frit A and Frit B based glasses.[9,10] These results coupled with visual observations and SEM/XRD results, suggest that the compositional changes recommended may provide higher actinide solubility limits without compromising durability as measured by the PCT.

Table 11. Normalized Releases for Select Alternative Pu Glasses (g/L)

Glass	NL [B] (g/L)	NL [Si] (g/L)	pH
EA	16.695	3.922	11.85
Frit B	0.025	0.013	7.50
Fe_2O_3 Based #2	0.024	0.026	6.94
High Ln_2O_3 #2 Mod	0.021	0.014	7.59
High Ln_2O_3 #4 Mod	0.020	0.011	7.54

4.4 Plutonium Glass Fabrication

Based on the surrogate test results, the High Ln_2O_3 #2 Mod glass was selected for follow-on plutonium glass fabrication. The surrogate work showed that this glass produced a homogeneous glass at high HfO_2 loadings with durability (as measured by the PCT) equivalent to or better than the reference Frit B composition. This composition was also in the "recommended glass forming region" from the literature review and analyses conducted in this study. This composition was selected over its "formulation cousin" (High Ln_2O_3 #4 Mod) because the relative lanthanide constituent composition was more balanced. The High Ln_2O_3 #2 Mod composition was at this point dubbed "Frit X" to coincide with previous LaBS frit designations.

The Frit X composition was prepared and analyzed prior to plutonium glass fabrication. Duplicate measurements were made using ICP-AES on the digested glass. All frit elements were found to be within ±10% of the targeted values. The measured boron value was approximately 9% lower than targeted indicating potential boron volatility. The sum of oxides for the measurements was approximately 98 wt % indicating good elemental recovery for the analyses. The measured values (average of the duplicate measurements) vs. targeted are shown in Table 12.

Table 12. Measured vs. Targeted Composition for Frit X used in Pu Glass Fabrication

Oxide	Targeted (wt %)	Measured (wt %)
Al_2O_3	10.0	10.4
B_2O_3	13.0	11.8
Gd_2O_3	13.5	13.6
HfO_2	7.0	6.6
La_2O_3	19.0	18.9
Nd_2O_3	15.0	13.9
SiO_2	20.0	20.3
SrO	2.5	2.6

The plutonium oxide material was obtained from Actinide Technology Section personnel. Analyses were conducted to determine the actinide isotopic distribution as well as screen for the presence of any gross impurity levels in the material. The results of these analyses are detailed elsewhere..[23]

The PuO_2 glass batches were prepared and melted as described in Section 2.3.2. The resulting glass appeared homogenous when visually examined in the crucible. Quenching of the glass was found to be ineffective in facilitating glass removal from the crucible (i.e., glass did not crack away from the crucible). Thus, the glass was not able to be removed from the crucible via routine means and "hammering" of the glass from the crucible was required. This resulted in pieces of glass (cullet) for follow-on analysis. This made it impractical to distinguish where the piece of glass originated with respect to the crucible melt. This precluded the ability to quantify any stratification of PuO_2 that may have occurred in the glass melt. Previous analyses by Vienna, et al. identified stratification of PuO_2 in plutonium loaded LaBS glasses fabricated in relatively small static crucible melts.[6] Follow-on testing should be performed to assess stratification of PuO_2 in this glass.

4.5 Plutonium Glass Characterization

4.5.1 SEM and XRD Analyses

A sample of the Pu-containing Frit X glass was submitted for XRD and SEM analyses. The XRD analysis indicated that there was some crystalline PuO_2 in the glass (Figure 11). Consistent with the XRD scan, the SEM analyses showed the presence of some undissolved PuO_2 particles with a disk-like morphology (Figure 12). This observation was consistent with previous microscopy analyses on Pu loaded Frit B glass.[23] It should be noted that the relative amount of undissolved PuO_2 looked to be less in the Frit X composition when compared to the previously analyzed Frit B composition. This was consistent with the expected enhanced PuO_2 solubility afforded by the Frit X composition. As mentioned previously, it is expected that stirring and/or co-grinding of the frit and PuO_2 would likely enhance dissolution. A second crystalline phase was observed with a very unique "star-like" morphology (Figure 13). This phase was in the glass with slightly less abundance than the undissolved PuO_2 phase. The phase was present either as well-developed "stars" (Figure 13) or as smaller "triangular" crystals (likely the early formation of the star-like crystals). The EDS spectra (Figure 13) of the star-like crystals indicated the presence of both Pu and Hf implying that these crystals were a solid solution of PuO_2 and HfO_2. These crystals likely formed during cooling of the glass and nucleated on the glass surface and/or at the crucible wall. The relative durability of this solid solution may be of special interest since the phase contains both PuO_2 and a neutron absorber (HfO_2). The potential to intentionally precipitate this phase in the glass may offer the potential for a waste form with enhanced durability. Initial testing to achieve this result was conducted in this study and is detailed below (see Section 4.6).

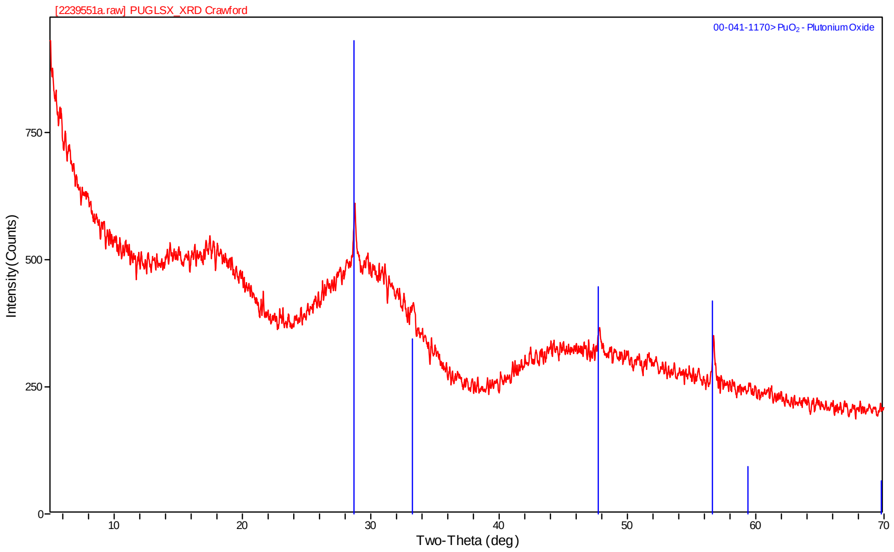


Figure 11. XRD scan of plutonium Frit X glass showing undissolved PuO_2.

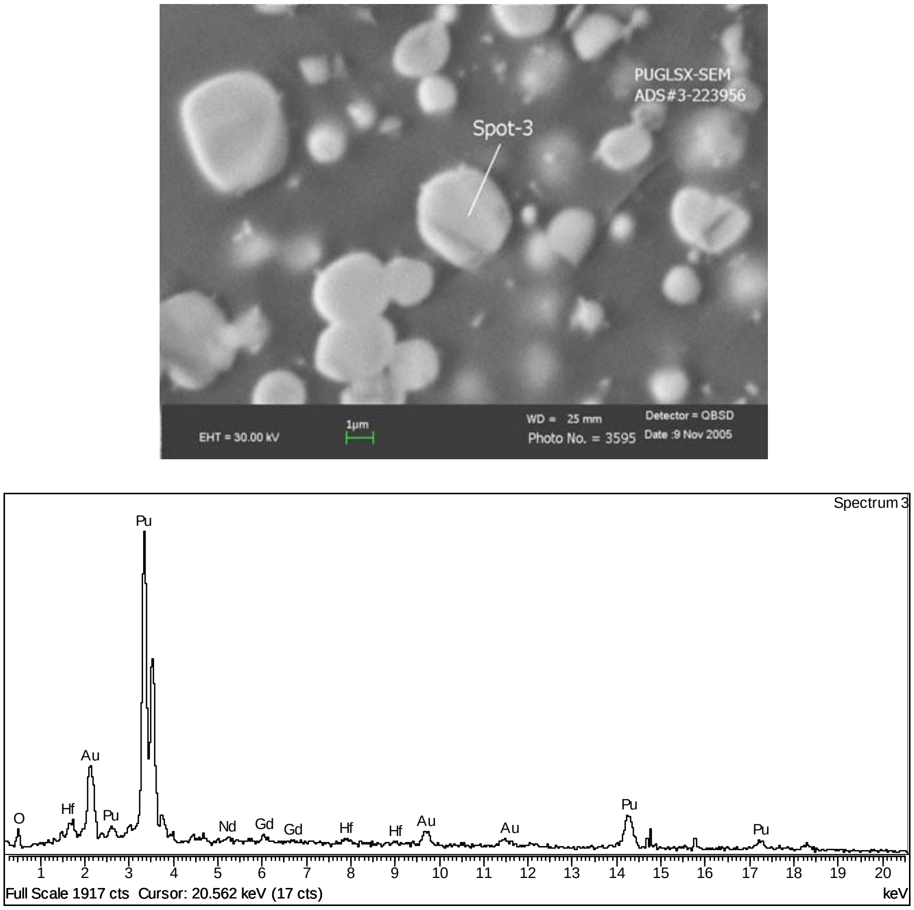


Figure 12. SEM micrograph and corresponding EDS spectra showing undissolved PuO_2 in the Frit X glass.

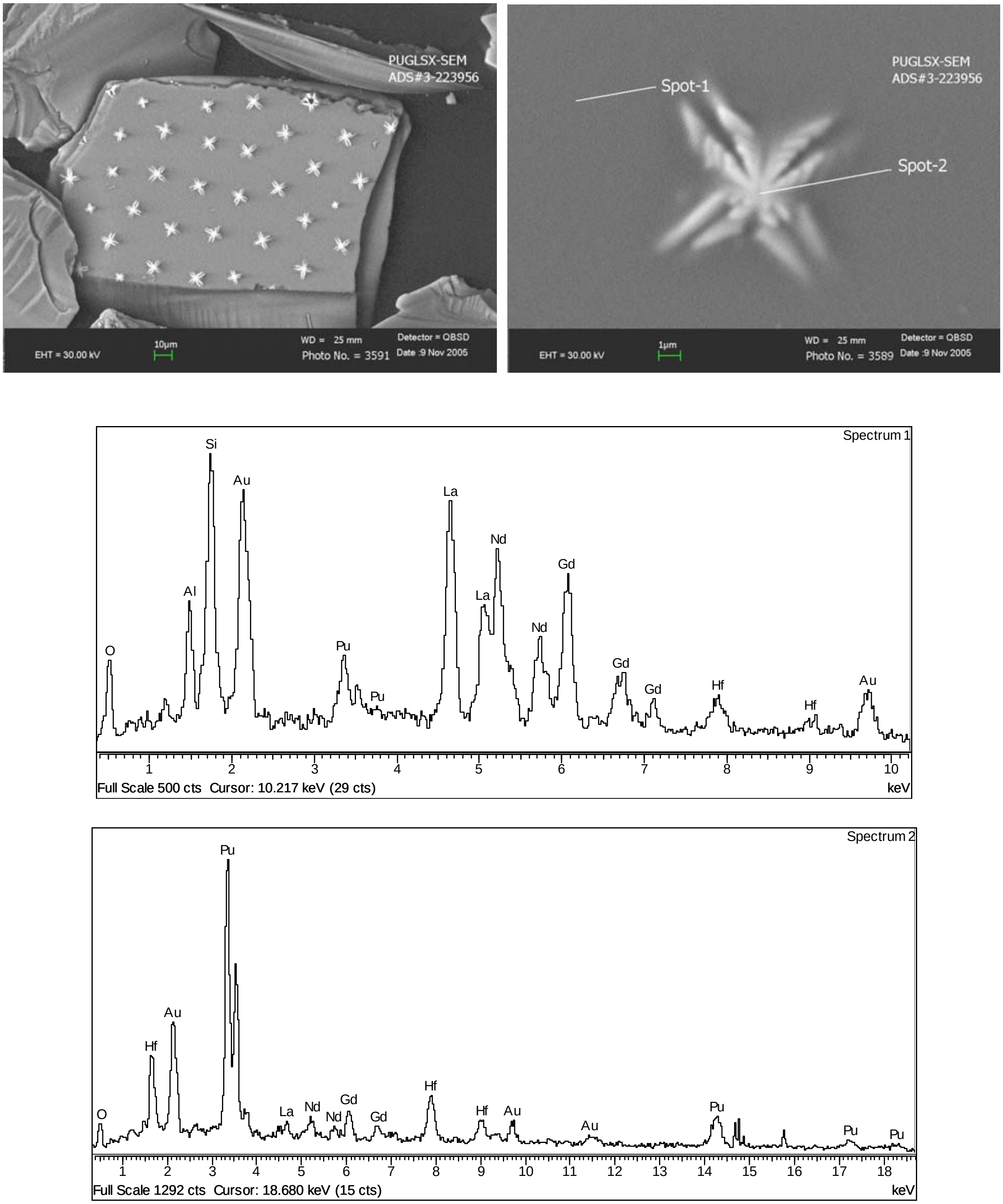


Figure 13. SEM micrograph and corresponding EDS spectra showing PuO_2-HfO_2 phase in the Frit X glass.

4.6 Glass Heat Treatment

Concurrent with the formulation development efforts, melter testing with the Frit B composition using HfO_2 as a surrogate for plutonium was also pointing to hafnium solubility and liquidus temperature issues. At this point, it was evident that at these high hafnium oxide concentrations, the solubility of hafnium oxide was exceeded in the Frit B glass. The use of zirconium oxide as a surrogate for PuO_2 was evaluated and determined to be an adequate simulant for the melter testing. Crucible scale tests using ZrO_2 added to the glass on an equivalent molar basis to PuO_2 resulted in a homogenous glass and melter testing commenced using this composition. During melter testing, however, there were some issues with glass draining from the melter. During one test, the drain tube plugged and it was necessary to remove the plugged section of the drain tube to continue operations. Glass was removed from the drain tube and submitted for SEM analysis. It was obvious from visual examination that glass devitrification had occurred in the drain tube. It was likely that lower temperatures where experienced in the drain tube during processing leading to devitrification. To support the melter testing and further assess the devitrification behavior of the surrogate Frit B glass (ZrO_2 as a surrogate for PuO_2), several isothermal heat treatments were conducted on the glass for subsequent analysis.

The surrogate Frit X composition (HfO_2 as a surrogate for PuO_2) was also subjected to isothermal heat treatments. There were three reasons for this testing. The first was to assess the devitrification behavior to compare to the reference Frit B composition. The second was to assist in defining a temperature window for heat treating the plutonium glass to intentionally form the PuO_2-HfO_2 solid solution in the glass. The results of this testing would then be used as a guide for actual plutonium glass testing. A third reason was to provide additional insight into the possibility of lowering melt temperature.

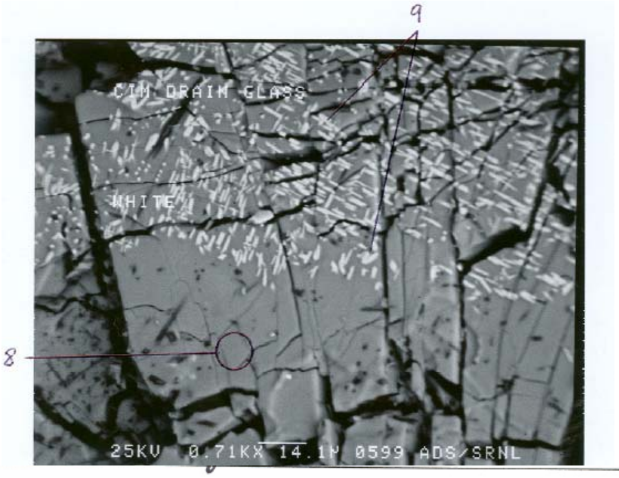
4.6.1 XRD and SEM Analyses

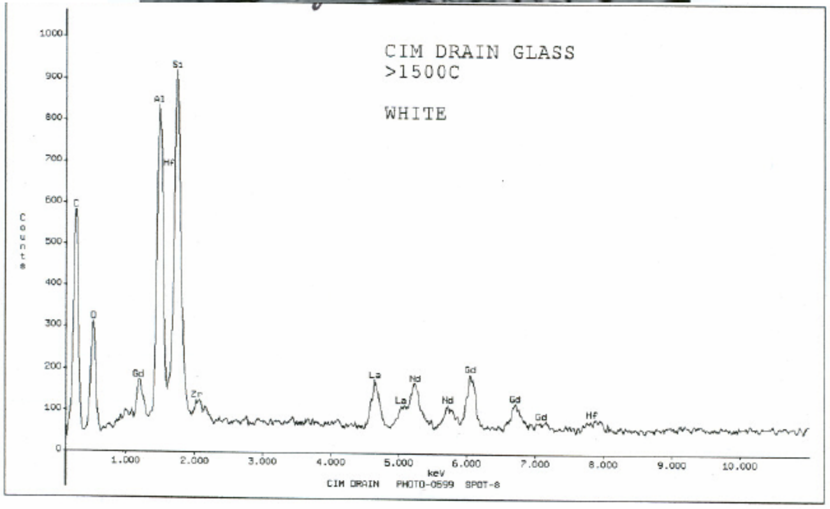
4.6.1.1 Surrogate Frit B Analyses

As indicated above, the surrogate plutonium glass that had crystallized in the drain tube of the CIM was examined by SEM. The micrographs indicated that rod like precipitates of HfO_2-ZrO_2 (where ZrO_2 was the surrogate for PuO_2) had formed in the glass. The precipitates were often found at right angles to each other (Figure 14). These rod shaped precipitates, and the associated box-like precipitation pattern, may participate in microcracking as the glass along the precipitate grain boundary exhibits microcracking.

The rod shaped precipitate morphology appeared in internal surfaces of the broken glass while irregular plate-like morphology crystals appeared on the surface. The chemistry of the rod shaped precipitates and the plate-like crystals was similar.

Glasses that had poured from the CIM before it plugged were heat treated at 1350° C and 1400° C for 24 hours to determine if devitrification had occurred in the CIM drain tube. The same flake and rod shaped ZrO_2-HfO_2 precipitates were visible in both devitrified samples. The same box-like precipitation pattern was observed for the rod-shaped precipitates in both samples. In the 1400° C sample there is evidence that the rod shaped precipitates grow from individual spherical precipitates of HfO_2-ZrO_2 like the spherical disk-like phase observed in the Pu glasses (Figure 15).





CIM DRAIN PHOTO-0599 SPOT-8

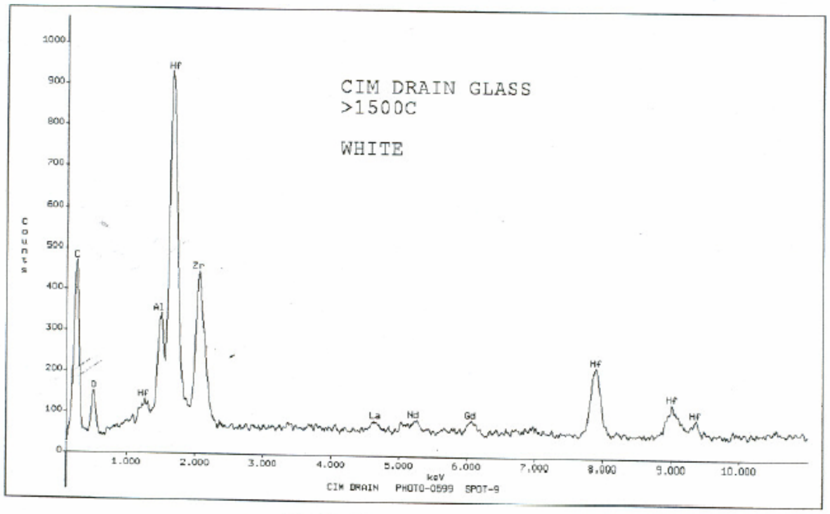


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Figure 14. SEM micrograph and corresponding EDS spectra of surrogate Frit B glass from the CIM drain tube showing HfO_2-ZrO_2 phase glass precipitated in the glass.

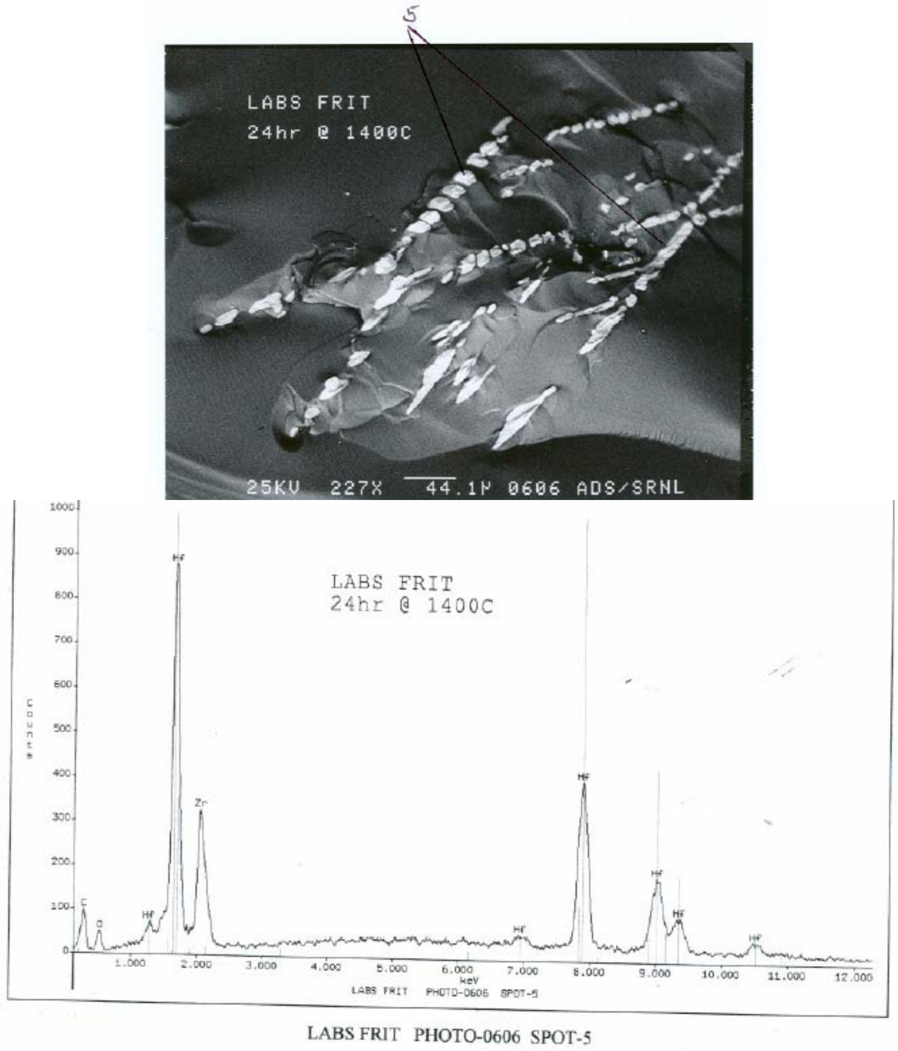


Figure 15. SEM micrograph and corresponding EDS spectra of surrogate Frit B glass from CIM testing heat treated at 1400° C.

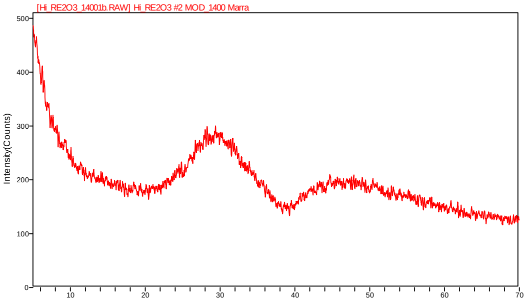
4.6.1.2 Surrogate Frit X Analyses

A series of isothermal heat treatments was conducted on the surrogate Frit X composition (HfO_2 as a surrogate for PuO_2) to assess the devitrification behavior of the glass. Heat treatments were conducted for 24 hours at 1400° C, 1350° C, 1300° C, 1250° C, 1200° C, 1100° C, 1000° C, and 900° C. Samples were submitted for XRD analysis. The XRD scans are shown in Figure 16.

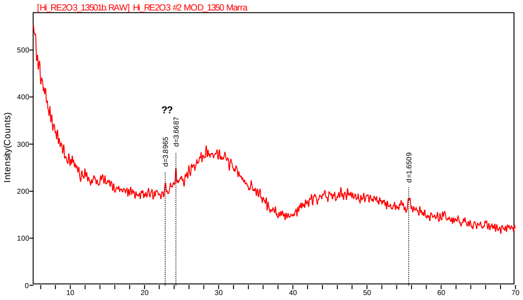
The XRD results for the glass sample heat treated at 1400° C indicated that the glass was amorphous (or free of crystals to the detection limit of 0.5 vol %). Additionally, only a few reflections with very low intensity were found in the 1350° C heat treated sample. These low intensity peaks could not be indexed to a known crystalline phase. These results indicated that the liquidus temperature behavior of the Frit X glass was markedly improved over the reference Frit B glass. This should facilitate melting the Frit X glass at a lower temperature and an expected improvement in processing in the CIM (e.g., precluding drain tube pluggage).

The XRD scans of the samples heat treated at 1200, 1250, 1300 and 1350° C showed that the thermal treatments caused hafnium oxide to be precipitated in the glass. The relative amount of HfO_2 increased as the heat treatment temperature was decreased. These results indicated that there was a relatively large window where a solid solution of PuO_2-HfO_2 could be potentially precipitated in the glass via post-melting thermal treatment. SEM analysis was conducted on a sample subjected to the 1200° C isothermal treatment (Figure 17). The micrographs clearly show the formation of a well-developed HfO_2 phase in the glass with a plate-like morphology. A finer rod-like phase was also observed (Figure 18). There were some indications that the finer, rod-like crystals were actually less-developed HfO_2 crystals. A similar rod-like phase was observed in the surrogate Frit B glass samples obtained from the CIM drain tube and samples heat treated at 1350 and 1400° C.

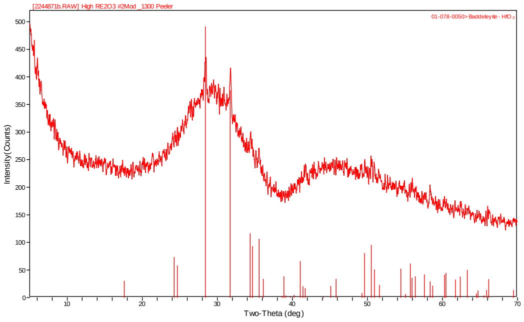
The XRD results for the surrogate Frit X samples heat treated at 1000 and 1100° C indicated that in this temperature range various mixed-rare earth oxides formed in the glass in addition to HfO_2. The sample heat treated at 900° C showed only very minor peaks that corresponded to mixed-rare earth oxide phases.



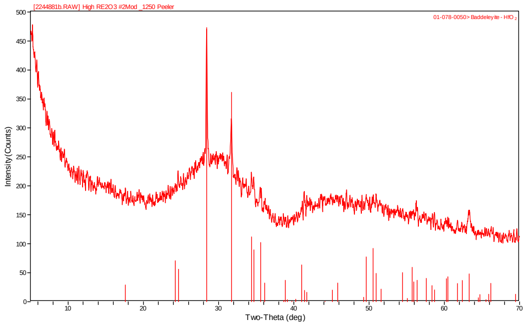
1400° C



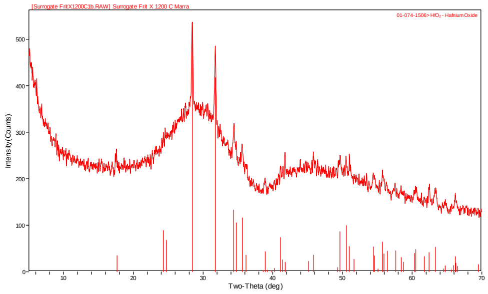
1350° C



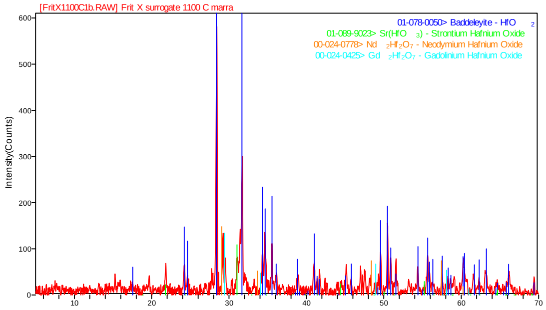
1300° C



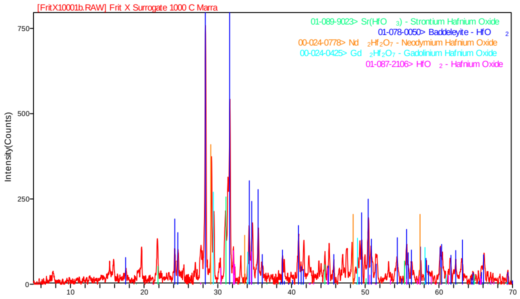
1250° C



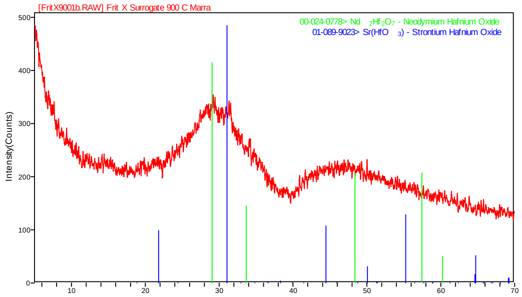
1200° C



1100° C

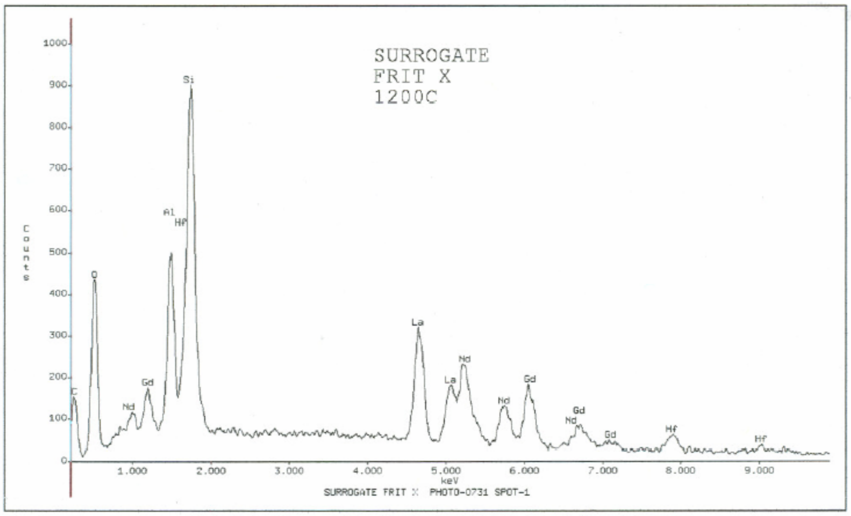


1000° C

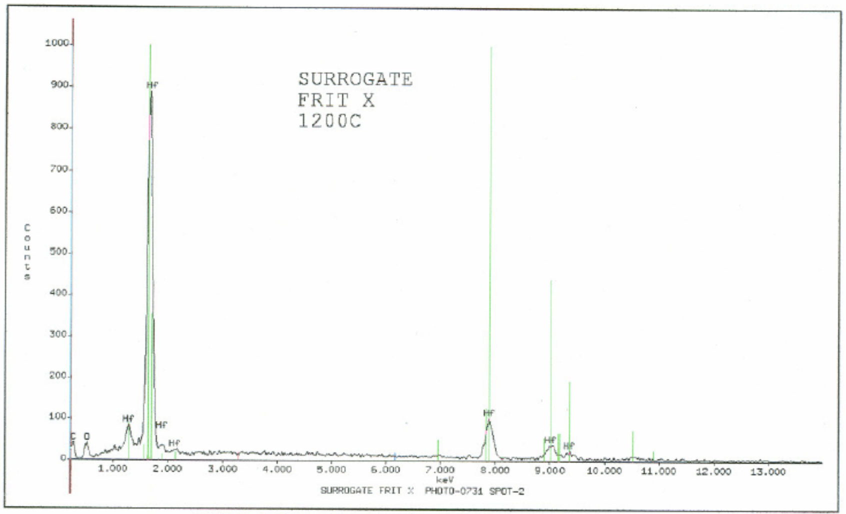


900° C

Figure 16. XRD Scans for heat treated surrogate Frit X glass.

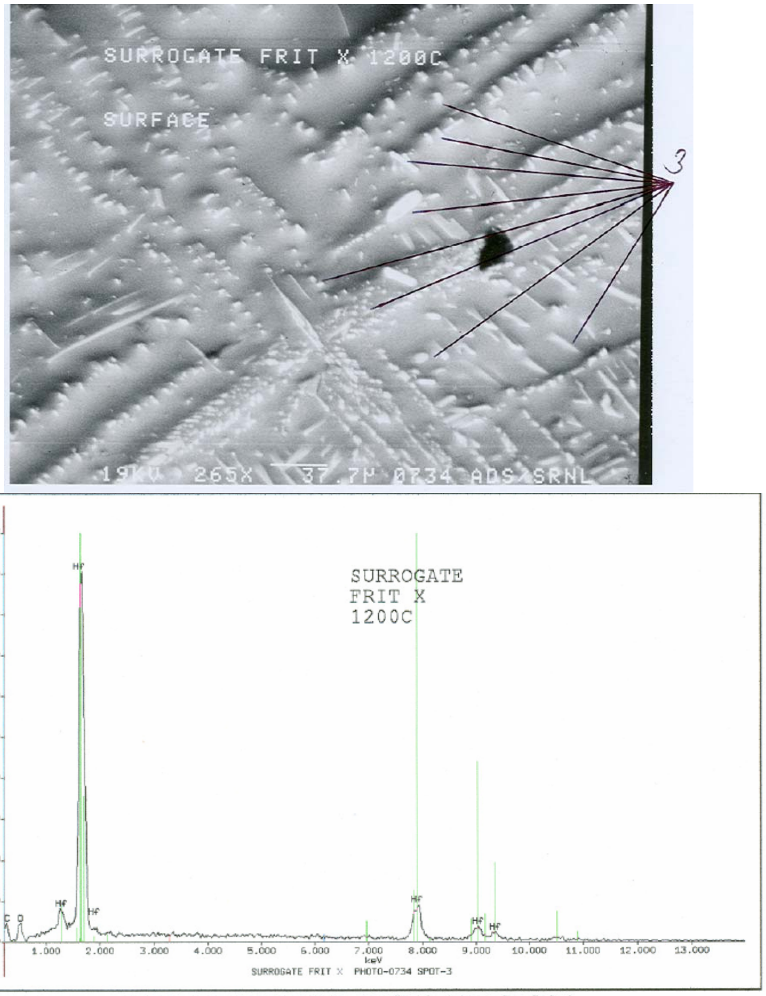


SURROGATE FRIT X PHOTO-0731 SPOT-1



SURROGATE FRIT X PHOTO-0731 SPOT-2

Figure 17. SEM micrograph and corresponding EDS spectra showing HfO_2 phase precipitated in the surrogate Frit X glass after heat treatment at 1200° C.



SURROGATE FRIT X PHOTO-0734 SPOT-3

Figure 18. SEM micrograph and corresponding EDS spectra showing fine HfO_2 phase precipitated in the surrogate Frit X glass after heat treatment at 1200° C.

4.6.1.3 Plutonium Frit X Glass Analyses

Based on the results of the surrogate heat treatment testing, the plutonium-containing Frit X glass was isothermally heat treated to evaluate the potential for intentionally precipitating the PuO_2-HfO_2 crystalline phase. Due to an operational issue with the primary radioactive high temperature furnace, a secondary furnace was utilized for heat treating the glass. This back-up furnace was limited to a maximum operating temperature of 1200° C. This temperature was at the low end of the “window” determined in the surrogate testing for precipitating HfO_2 in the glass but it was still deemed worthwhile to perform a heat treatment on the Pu Frit X glass at this temperature. A sample of the Pu-bearing Frit X glass was heat treated for about 10 hours at 1200° C. Sub-samples of the heat treated glass were analyzed by SEM and XRD.

The SEM results showed that significant crystallization occurred in the glass (Figure 19). The EDS spectra for the plate-like crystalline phase (spot 5) indicated that this phase was likely a mixed-rare earth oxide that was devoid of hafnium. A finer-sized crystalline phase (spot 7) was also observed and appeared to be enriched in plutonium and included all of matrix glass elements. In an effort to better quantify the composition of the enriched plutonium phase, the beam current was reduced on the microscope to minimize the penetration through the phase and into the matrix glass. This was somewhat successful and the resulting EDS spectra indicated that this phase was primarily plutonium oxide (Figure 20). There appeared to be continued beam penetration as pronounced silicon and aluminum peaks were again observed. The "shoulder" on the primary silicon peak implied that this phase also included Hf in the composition. The XRD pattern for the heat treated Pu-containing Frit X glass showed a predominance of mixed-rare earth oxide (Figure 21). It was evident from these analyses that heat treatment at 1200° C did not provide the desired result of forming an abundant PuO_2-HfO_2 phase in the glass. Follow-on work will be conducted at higher thermal treatment temperatures in an attempt to achieve this result.

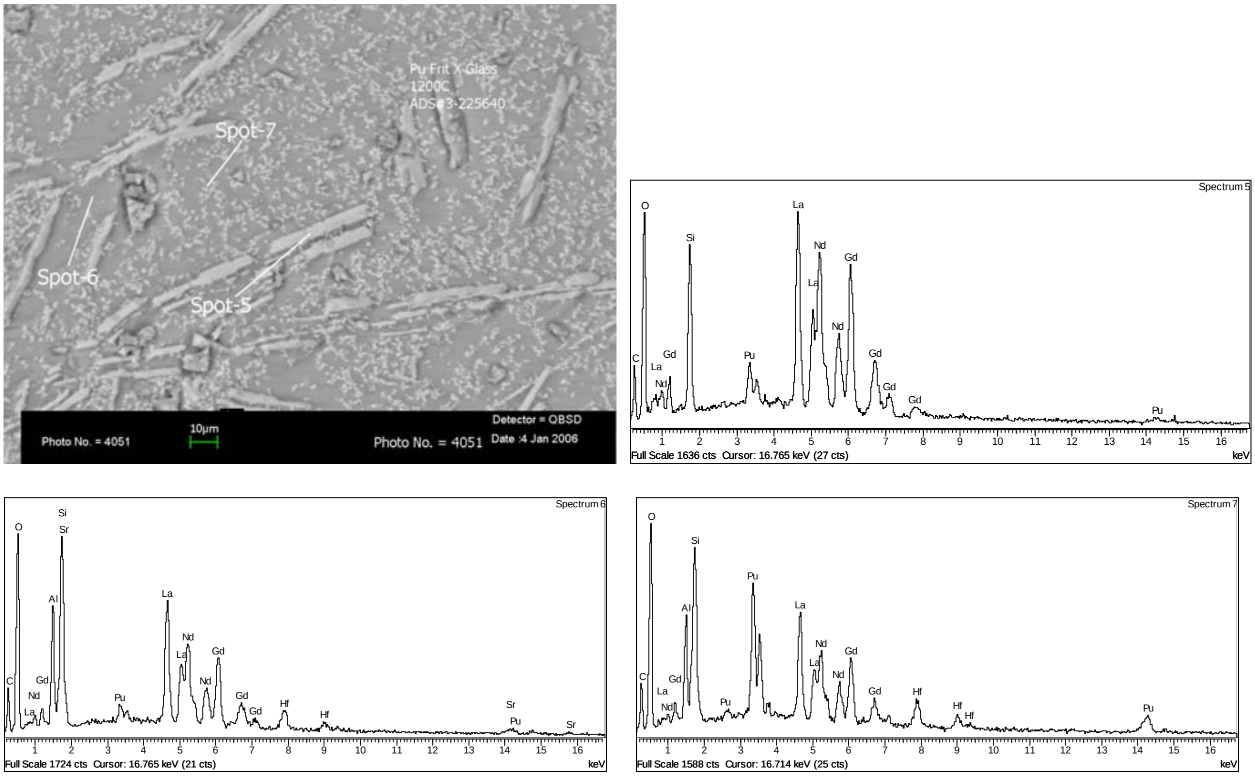


Figure 19. SEM micrograph and corresponding EDS spectra showing HfO_2 phase precipitated in the plutonium-containing Frit X glass after heat treatment at 1200° C

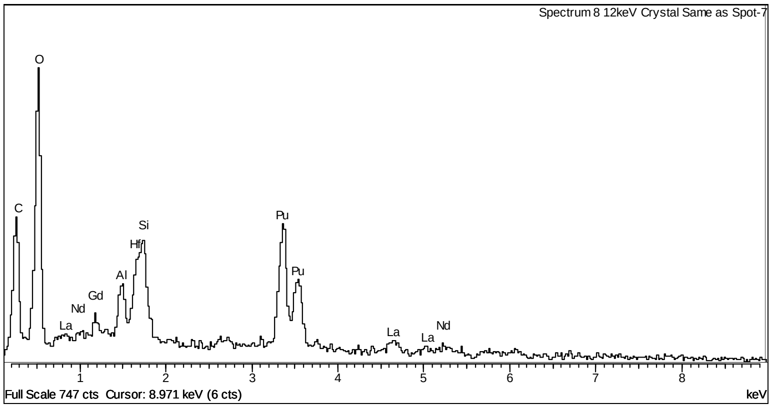
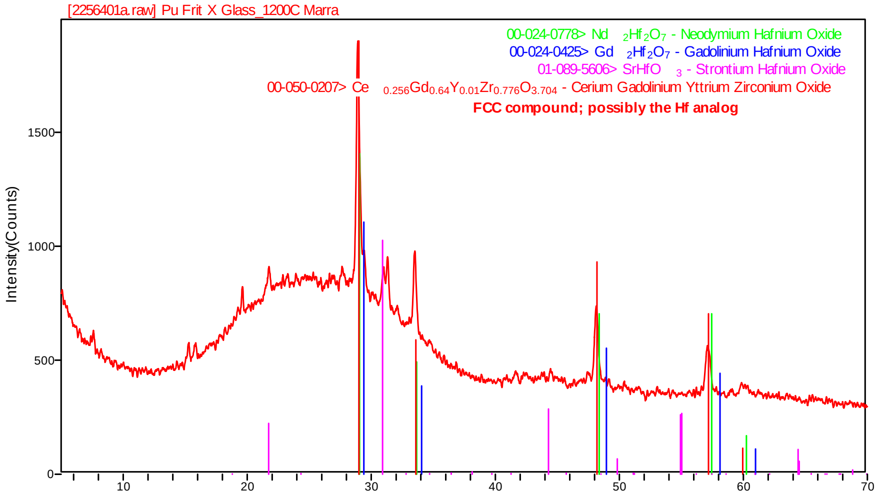


Figure 20. EDS spectra of spot 7 in Figure 4-11 with a beam current of 12 keV



Note: The Cerium Gadolinium Yttrium Zirconium Oxide phase is not possible to form with the composition of glass. However, a similar phase with substituted lanthanides in this stoichiometry is possible.

Figure 21. XRD Scan for plutonium-containing Frit X glass heat treated at 1200° C.

5.0 CONCLUSIONS

Analyses and testing to develop alternative glass compositions for the disposition of PuO_2 led to the following conclusions:

- A phase equilibrium approach and glass science principals were successfully utilized to identify candidate alternative LaBS glass formulations. This methodology resulted in the identification of a formulation that moved the composition from a potential region of phase separation and into a region near a low melting point eutectic. This composition was dubbed the LaBS – Frit X composition.

- The Frit X composition was shown to have durability (as measured by the PCT) equivalent to the reference LaBS – Frit B composition and significantly better than the EA glass.

- Enhanced component solubility was observed in surrogate and PuO_2 testing with the Frit X composition when compared to the reference Frit B composition.

- Improved devitrification behavior was observed with the Frit X composition. This will facilitate melter processing and could result in a lower glass melting temperature.

The presence of a PuO_2-HfO_2 solid solution phase was identified in the Pu-containing Frit X glass upon initial fabrication. This could result in the potential to improve the plutonium leach performance in the repository by the formation of a highly insoluble phase with inherent neutron absorber.

6.0 RECOMMENDATIONS/PATH FORWARD

In this study, a viable alternative LaBS glass composition (Frit X) was identified. Further detailed testing should be conducted on this composition to provide data to support repository modeling and to support project design activities. Specifically, the suite of performance tests currently being conducted on the reference Frit B composition should be conducted on the Frit X composition to provide the necessary data for repository modeling. The potential to form a PuO_2-HfO_2 phase in the glass should also be further pursued as a potential means to improve waste form performance. Additionally, as the feed stream chemistry destined for disposition via vitrification is better defined, a thorough glass formulation variability study should be performed to demonstrate that feed variations can be accommodated in the glass. Finally, this composition should be utilized in melter testing to support project design initiatives.

Consistent with waste glass formulation practices, test data with the Frit X composition should be reviewed to evaluate if any future iterative composition changes are deemed to be beneficial. The phase equilibria approach developed for this effort should be a valuable tool in these assessments.

7.0 ACKNOWLEDGEMENTS

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