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Homogeneous Glass Processing Region Defined for a Lanthanide Borosilicate Glass Composition for the Mobilization of Plutonium Using Thorium as a Surrogate (U)

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Summary

A ternary diagram showing the homogeneous glass processing region of a base frit, rare earth oxide and thorium oxide has been developed for a residence temperature of 1475° C. Thorium oxide was used as a plutonium surrogate. All ThO_2 glasses that were processed included a 1:1 mole ratio of Th to Gd. Gadolinium is added to the glass as a neutron absorber. Forty individual glass compositions were melted at 1475° C for 4 to 6 hours with periodic stirring. Two glasses (B-20-25 and B-25-25) were processed with a ThO_2 loading of 25 weight percent (oxide) without amorphous phase separation or crystalline species detected by X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM) or Transmission Electron Microscopy (TEM). These were processed with 55 weight percent frit, 20 weight percent rare earth oxides and 50 percent frit, 25 percent rare earth oxides.

Crystalline species that formed outside of the homogeneous glass processing region due to solubility limits or insufficient processing temperature were identified. Amorphous phase separation was detected and examined by TEM at high ThO_2 loadings (20 to 30 weight percent oxide). The base frit was able to dissolve up to 65 weight percent rare earth oxides when thorium oxide was not present.

Durability testing will be performed on three glasses from three different regions of the homogeneous glass processing region. Product Consistency Test (PCT) results are pending and will be added to this document under a future revision.

Introduction

In support of the Fissile Material Disposition Program, the Savannah River Technology center (SRTC) is evaluating a lanthanide borosilicate (LaBS) glass composition for possible plutonium immobilization. This glass has been shown to accommodate up to 10 weight percent Pu along with rare earth elements (REE)[1], which may be used as neutron absorbers (Gd). The durability of Pu-loaded LaBS glasses has been shown to be ~50x better than high level waste (HLW) glasses produced at the Defense Waste Processing facility (DWPF)[2]. Several different LaBS glass compositions have been processed with Th (a Pu surrogate) and Pu as glass formulation efforts strive to optimize the system. Initial LaBS glass composition contained PbO and BaO (for Am/Cm Demonstration Project) [2-3]. More recent compositions have removed the lead and barium, resulting in a glass composition without hazardous elements as defined by the Resource Conservation and Recovery Act (RCRA) [4]. This composition is represented in this study as 'B-24-17' and represents 15 elemental weight percent Th. This document summarizes the work performed to develop a compositional envelope around this composition with ThO_2 used as a plutonium surrogate in the LaBS glass without lead or barium. The resulting compositional envelope will then be tested with PuO_2 loadings in the glass.

Experimental

Glass compositions were batched in platinum crucibles with reagent chemicals in the oxide form with the exception of boron. The boron content was added as boric acid. Glasses were melted at 1475° C for 4-6 hours with manual stirring after ~2 hours at temperature. The ramp rate was 560° C/hr. As the melts were removed from the furnace, the crucibles were placed in a pan of water to 'shock' the glass from the crucible surface which allowed for total recovery of the processed glass. The compositional envelope was defined by varying the percentages of:

(1) Frit (Table I),
(2) Rare Earth (lanthanide) oxides, and
(3) ThO_2 (PuO_2 surrogate).

The base frit composition (renormalized components of B-24-17 without ThO_2 and rare earth oxides) did not change, but was used in decreasing amounts as the rare earth oxides and ThO_2 content increased.

Table 1. Base frit composition for the LaBS glass. Includes all components except lanthanides and actinides.

Oxide	Weight Percent
SiO_2	44.0
B_2O_3	17.7
Al_2O_3	32.5
SrO	3.8
ZrO_2	2.0

The rare earth contributors were lanthanum and neodymium with gadolinium, used as the neutron absorber. As the actinide content increased, the gadolinium content increased, maintaining a 1:1 atomic ratio with thorium. The amount of La and Nd decreased to compensate for the increase in Gd.

In order to bound the processing region, initial ratios of the three components were determined by previous experience with this system (both successful and unsuccessful melts). First, as homogeneous glasses were produced, new compositions with systematic increases in lanthanide and/or actinide loadings were attempted. Second, an equilateral triangle was used by placing two corners on successful melts, the third corner of the triangle determined a new compositon to be processed. Finally, when an outline of a processing region was apparent, compositions near the boundary (between the homogeneous and non-homogeneous glass region) were tested to better determine the boundary line.

Glass formulations were evaluated for homogeneity by XRD, SEM and TEM (for amorphous phase separation). Three homogeneous glasses from different regions of the processing range were analyzed by sodium peroxide fusion followed by Inductively Coupled Plasma - Atomic Emission Spectroscopy (ICP-AES) for chemical composition. The 7-day PCT for durability[5] were performed on these glasses to determine if the durability of the glasses changed significantly with respect to different lanthanide and/or thorium loadings.

Results and Discussion

The ternary diagram (Figure 1) shows the homogeneous glass forming region for the base glass, rare earth oxide (lanthanide content) and thorium oxide system at 1475° C. Table II shows the batch compositions and processing results of all glasses shown in Figure 1.

At high frit loadings (>75 weight percent), the glass was not processable due to the frit being highly refractive. Over 94 percent of the frit is composed of SiO_2, B_2O_3 and Al_2O_3. The phase diagram for these three components indicates that the melting point for this composition is ~1650° C[6]. Crystalline species in this part of the ternary diagram were found to be aluminum borate. All rare earth oxides and thorium oxide were incorporated into a glassy phase. Crystalline species or undissolved oxides containing these elements were not detected by XRD. As the frit drops below 75 percent, the fluxing affects of the rare earth elements effectively lowers the melting to allow processing in a bushing melter.

Table II. Batched compositons of glasses that were tested for durability in weight percent oxide.

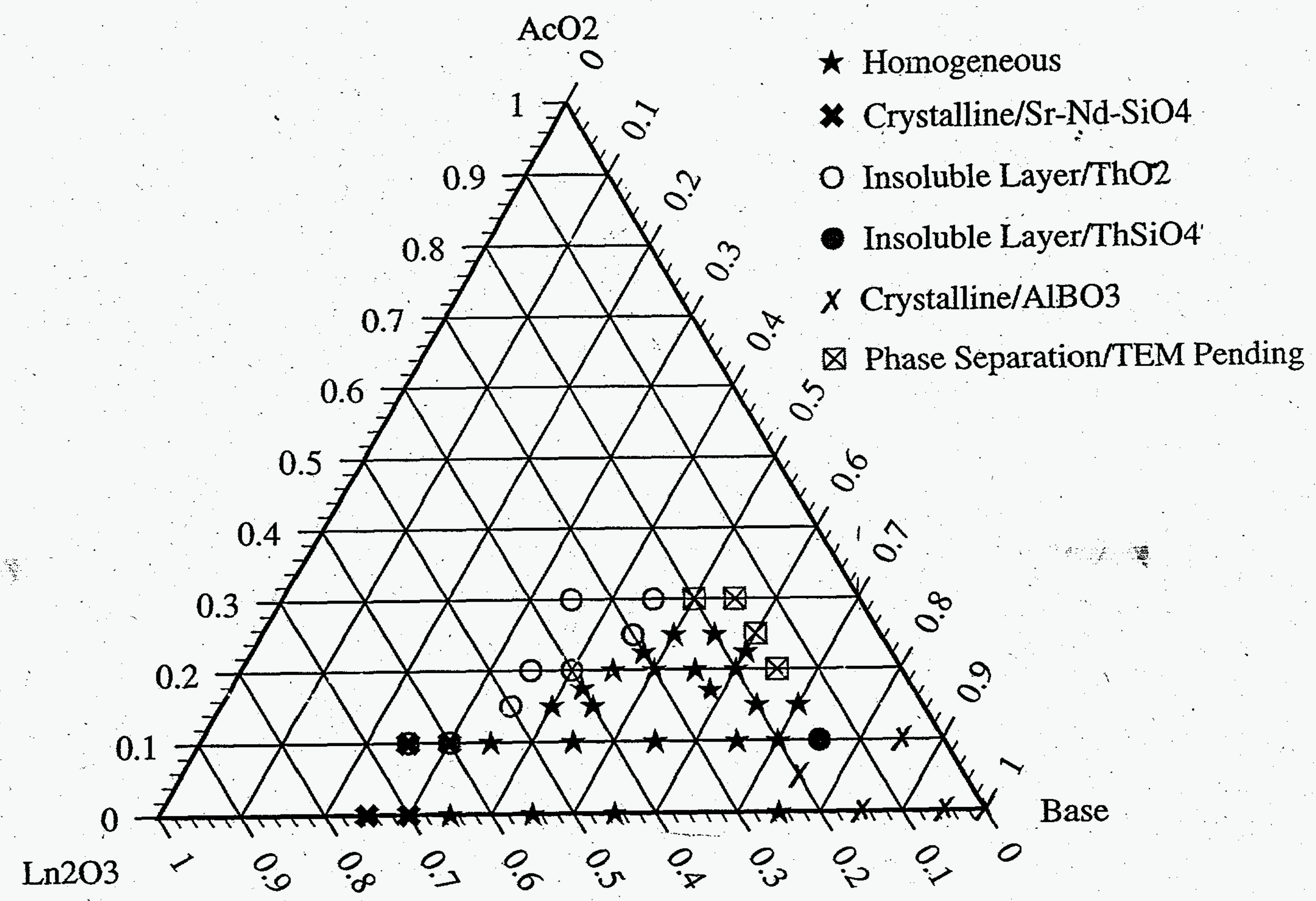
Glass Id	Base Frit	REE	ThO_2	Homogeneous?
B-24-17	59	24	17	YES
Base	100	0	0	$AlBO_3$
B-5-0	95	5	0	$AlBO_3$
B-5-10	85	5	10	$AlBO_3$
B-15-0	85	15	0	$AlBO_3$
B-25-0	75	25	0	YES
B-45-0	55	45	0	YES
B-55-0	45	55	0	YES
B-65-0	35	65	0	YES
B-75-0	25	75	0	Sr-Nd-SiO_4
B-70-0	30	70	0	Sr-Nd-SiO_4
B-15-10	75	15	10	$ThSiO_4$
B-20-5	75	20	5	$ALBO_3$
B-25-10 (PCT)	65	25	10	YES
B-35-10	55	35	10	YES
B-45-10	45	45	10	YES
B-55-10 (PCT)	35	55	10	YES
B-65-10	25	65	10	Sr-Nd-SiO_4†
B-60-10	30	60	10	Sr-Nd-SiO_4†
B-20-20	60	20	20	YES
B-25-20	55	25	20	YES
B-30-20	50	30	20	YES
B-45-20	35	45	20	ThO_2
B-40-20	40	40	20	ThO_2
B-35-20	45	35	20	YES
B-20-25	55	20	25	YES
B-25-25 (PCT)	50	25	25	YES
B-30-25	45	30	25	ThO_2
B-20-30	50	20	30	A.P.S.††
B-25-30	45	25	30	ThO_2
B-35-30	35	35	30	ThO_2
B-15-30	55	15	30	A.P.S.††
B-15-25	60	15	25	A.P.S.††
B-15-20	65	15	20	A.P.S.††
B-17.5-22.5	60	17.5	22.5	YES
B-20-10	70	20	10	YES
B-15-15	70	15	15	YES
B-20-15	65	20	15	YES
B-45-15	30	45	15	YES
B-50-15	35	50	15	ThO_2

† Also contained a ThO_2 layer on the bottom of the melt pool.

††Amorphous Phase Separation.

At high rare earth oxide loadings (>65 weight percent oxide) the solubility limit of rare earth oxides (only, no thorium oxide) was exceeded. XRD detected strontium-rare earth-silicates. As thorium oxide was added, the combined solubility limit of rare earths and thorium decreases. The highest combined solubility (Th and REE) reached 65 weight percent (10 percent ThO_2, 55 percent Ln_2O3). At the highest ThO_2 loading (25 weight percent oxide), the combined solubility (Th and REE) was only 50 weight percent. The indication of solubility limits being exceeded was the formation of a thorium oxide layer on the bottom of the melt pool and/or crystalline strontium-neodymium silicates throughout the melt.

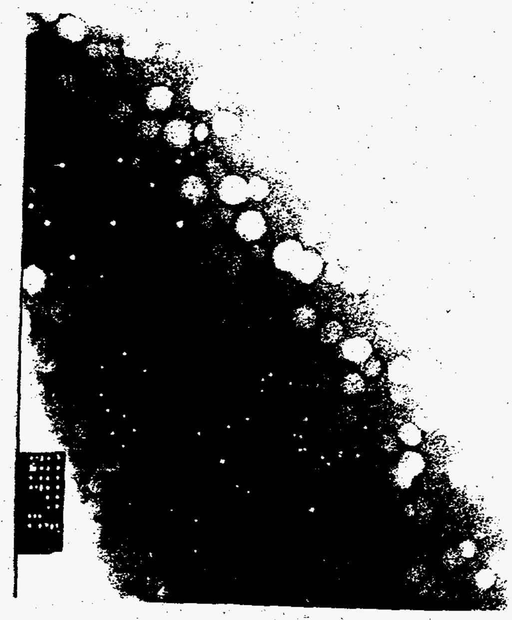
Figure 1. Ternary diagram of LaBS glass compositions with ThO_2 loadings.



Glass compositions were attempted with 30 weight percent thorium oxide with 15 and 20 weight percent Ln_2O_3. These glasses had an opalesent appearence indicative of amorphous phase separation. XRD and SEM could not identify any crystalline structures. TEM detected the presence of silicon-rich droplets 20 to 30 nm in diameter. Figure 2 is TEM micrograph of the amorphous phase separation of the B-15-30 glass. Unlike HLW glass, the microstructure of the amorphous phase separated LaBS glass is quite stable. Phase separated glasses containing sodium (i.e. HLW glass) is vulnerable to electron beam attack during

TEM analysis. No beam damage was observed in the B-15-20 glass as a result of prolonged electron beam exposure (~5 minutes).

Figure 2. TEM micrograph of a phase separated glass (B-15-30) showing Si-rich droplets that are 20-30 nm in diameter.



Durability
The three glasses will be analyzed and tested for durability are indicated in Table II by "PCT". The durability, based on normalized releases of boron and silicon, of the three glasses will be compared to the Approved Reference Material - 1 (ARM) glass[7]. Durability results are pending and will be incorporated into this document under a future revision.

Conclusions

A ternary diagram showing the homogeneous glass processing region of a base frit, rare earth oxide and thorium oxide has been developed at 1475° C. Thorium oxide was used as a plutonium surrogate. All ThO_2 glasses processed included a 1:1 mole ratio of Th to Gd. Gadolinium is added to the glass as a neutron absorber. Forty individual compositions were melted at 1475° C for 4 to 6 hours with periodic stirring. Two glasses (B-20-25 and B-25-25) were processed with a ThO_2 loading of 25 weight percent (oxide) without amorphous phase separation or crystalline species. These were processed with 55 weight percent frit, 20 weight percent rare earth oxides and 50 percent frit, 25 percent rare earth oxides.

Crystalline species that formed outside of the homogeneous glass processing region due to solubility limits or insufficient processing temperature were identified. Amorphous phase separation was detected and examined by transmission electron microscopy (TEM) at high ThO_2 loadings (25 to 30 weight percent oxide). The base frit was able to dissolve up to 65 weight percent rare earth oxides without thorium oxide.

Durability testing was performed on three glasses from three different regions of the homogeneous glass processing region. PCT results are pending and will be added to this document under a future revision.

References

1. Vienna, J.D., et. al., "Plutonium Dioxide Dissolution in Glass," PNNL-11346, Pacific Northwest National Laboratory, Richland, WA, (September 1996).

2. Bibler, N.E., Ramsey, W.G., Meaker, T.F. and Pareizs, J.M., "Durabilities and Microstructures of Radioactive Glasses for Immobilization of Excess Actinides at the Savannah River Site", Materials Research Society Symposia Proceedings, Vol. 233, pp. 333-336, Materials Research Society, Pittsburgh, PA (1995).

3. T.F. Meaker, "Effects of Periodic Manual Stirring and Uranium Addition on Surrogate Plutonium Glass Processing," WSRC-TR-96-0321, Westinghouse Savannah River Company, Aiken, SC, (September, 1996)

4. T.F. Meaker, "Compositional Development of a Lanthanide Borosilicate Glass for Plutonium Immobilization Without Listed RCRA Materials (Lead and Barium) (U)," WSRC-TR-96-0322, Westinghous Savannah River Company, Aiken, SC, (September 1996).

5. C.M. Jantzen, N.E. Bibler, D.C. Beam, and W.G. Ramsey, "Nuclear Waste Glass Product Consistency Test (PCT) - Version 7.0 (U)," USDOE Report WSRC-TR-90-539, Rev. 3, Westinghouse Savannah River Co., Aiken, SC (June 1994).

6. Figure No. 763, Phase Diagrams for Ceramists, American Ceramic Society, (1996).

7. Mellinger, G.B., and Daniel, J.L., "Approved Reference and Testing Materials for Use in Nuclear Waste Management Research and Deveolopment Programs," U.S. DOE Report PNL-4955-2, Materials Characterization Center, Batelle Pacific Northwest Laboratory, Richland, WA, (December 1984).