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**Compositional Development of a Plutonium Surrogate
Glass Without Listed RCRA Elements (Lead And Barium) (U)**

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Summary

A lanthanide borosilicate (LaBS) glass composition, being evaluated by the Savannah River Technology Center (SRTC) for plutonium disposition as part of the U.S. Department of Energy's (DOE) Office of the Fissile Materials Disposition (OFMD) program, has been processed with greater than 15 elemental weight percent thorium (a plutonium surrogate) without the presence of lead oxide in the glass. The glass composition is a result of several efforts to remove the lead by replacing it with strontium and sodium. The initial melts that included sodium and considerably lower aluminum resulted in visible phase separation.

Two homogeneous lead free melts have been processed. The first one replaced one-fifth of the total lead with Sr on a mole percent basis. Other changes included slightly less aluminum with increases in boron and silica. The second glass composition was exactly the same as the first with an additional 1:1 replacement of barium with strontium on a mole percent basis. This last composition contains no elements considered to be hazardous as defined by the Resource and Conservation Recovery Act (RCRA elements). The Product Consistency Test (PCT) results of these two homogeneous glass compositions show them to be slightly more durable than the original lanthanide borosilicate glasses (with lead) loaded with thorium.

Introduction

The LaBS glass composition soon to be in production for Am/Cm vitrification demonstration at the Savannah River Site (SRS) and presently being optimized for possible plutonium disposition has always contained a significant amount of lead oxide. Lead oxide acts as a very effective flux for silicate glasses, similar to oxides of alkali and alkaline earth elements. An added benefit provided by PbO is the increased durability of the glass compared to compounds of Na₂O and CaO in glass[1]. Furthermore, the increased density of the glass due to PbO allows for greater actinide loadings on a grams per cubic centimeter basis, effectively adding to the volume reduction of the glass waste form. All of these effects are apparent in the LaBS glass composition[2].

The durability of the lead containing LaBS glass has been shown to be approximately 50x more durable than typical glass produced at the Defense Waste Processing Facility (DWPF)[2], which contains significant amounts of Na₂O and CaO. The density of the LaBS glasses is ~1.7x that of the DWPF glass with waste loadings of ~0.45 grams Pu/cc glass. However, the repository at Yucca Mountain may not allow for the disposition of Pu loaded glass forms containing RCRA materials. This paper reports the development of surrogate glass compositions for Pu immobilization without Pb and Ba. The processability and product performance of these no-RCRA melts are compared to previous LaBS glass compositions with Pb and Ba.

Experimental

Compositional Development and Processing

Initial attempts to remove lead from the base LaBS composition used Sr and Na as a replacement. Strontium has an ionic nucleus very close in size to Pb and the same charge, therefore it is expected to process similarly. Sodium was added to replace the fluxing effect of lead. To compensate for the increased modifier (Na and Sr) content in the 'no-lead' glass, some aluminum was removed and replaced with two glass formers (Si and B). Table I compares this glass composition (No Pb-SrNa) with the base LaBS composition containing Pb and Ba.

All of the reported glass compositions targeted 15 elemental weight percent thorium and were batched with oxides with the exceptions of boric acid and thorium nitrate tetrahydrate. Melts were processed at 1450° C, unless otherwise noted, in platinum/rhodium crucibles. A platinum stir bar was used to manually stir the melt two to three times during the melt regime. Residual glass adhered to the stir bar after stirring was analyzed by X-Ray Diffraction (XRD) for homogeneity.[†] When crucibles were removed from the furnace, they were placed in approximately one inch of room temperature water to facilitate cooling and removal of the glass from the crucible. One glass was thermally treated to evaluate the effect (if any) of a slow (compared to quenched) cooling rate on the formation and/or promotion of amorphous phase separation using a controlled cooling schedule anticipated during an actual canister pour.

Table I. Glass compositions of the Base LaBS glass with and without lead (mole percent oxide).

<u>Oxide</u>	<u>Base LaBS</u>	<u>No Pb - Sr,Na</u>
SiO ₂	42.6	46.6
B ₂ O ₃	12.0	18.0
Al ₂ O ₃	24.0	14.0
ZrO ₂	1.0	1.0
La ₂ O ₃	3.0	3.0
Nd ₂ O ₃	1.4	1.4
Gd ₂ O ₃	3.4	3.4
ThO ₂	6.9	6.9
PbO	4.2	---
Na ₂ O	---	3.4
SrO	---	0.8
BaO	1.5	1.5

The no lead glass (No Pb - Sr,Na) was processed in duplicate and both were stirred with a platinum stir bar after 3.7 hours at 1450° C. A second stir, approximately 4.5 hours after reaching 1450° C was performed on both melts. The glasses were removed after 5.3 hours at temperature and quenched in water.

Compositional development continued producing two other compositions: The first glass, (No RCRA - Na) replaced both strontium and barium of the No Pb - Sr,Na melt (shown in Table I) with sodium on a 1:1 mole percent basis. The second glass (No Pb - Sr) removed all the sodium relative to the No Pb - Sr,Na melt (Table I) and increased the aluminum content to 20 mole percent. These changes were compensated for by adjusting the silica and boron content.

The as-batched (targeted) compositions of the "second generation" glasses are shown below (Table II). Both of these compositions were processed in duplicate (4 total melts) as previously described. All melts were stirred after 2 and 3.5 hours and removed after 5.0 hours.

[†] The residual glass should be representative of the melt at time of stirring.

Finally, to remove the barium in the No Pb - Sr melt (Table II), Ba was replaced with Sr on a 1:1 mole percent basis. This composition (No RCRA - Sr) is shown in Table III. This composition was processed in 6 different batches, of which one was a static melt (no stirring) at 1475° C for 3.4 hours. Different cooling rates were employed to assess the possibility of phase separation formation after processing. Melts 1,2 and 3 were water quenched as described above while melts 4 and 6 were cast into graphite molds and annealed at 570° C for 1 hour and then allowed to cool inside the annealing oven overnight. Two of the six were processed at 1425° C. These were slightly thicker during stirring but still processable (easily stirred).

Table II. Second generation LaBS glass composition without lead (mole percent oxide).

<u>Oxide</u>	<u>No RCRA - Na</u>	<u>No Pb - Sr</u>
SiO ₂	46.6	46.0
B ₂ O ₃	18.0	16.0
Al ₂ O ₃	14.0	20.0
ZrO ₂	1.0	1.0
La ₂ O ₃	3.0	3.0
Nd ₂ O ₃	1.5	1.2
Gd ₂ O ₃	3.4	3.5
ThO ₂	6.8	7.0
Na ₂ O	5.7	---
SrO	---	0.8
BaO	---	1.5

Table III. The LaBS glass composition containing no RCRA elements.

<u>Oxide</u>	<u>No RCRA - Sr</u>
SiO ₂	46.0
B ₂ O ₃	16.0
Al ₂ O ₃	20.0
ZrO ₂	1.0
La ₂ O ₃	3.0
Nd ₂ O ₃	1.2
Gd ₂ O ₃	3.5
ThO ₂	7.0
PbO	---
Na ₂ O	---
SrO	2.3
BaO	---

Durability

The Product Consistency Test (PCT) Method A[3] was used to assess the relative durability of three homogeneous glass compositions (base LaBS, No Pb - Sr, and No RCRA - Sr). The Savannah River Laboratory - Environmental Assessment (SRL-EA) glass[4] was also included for comparison. A dilution factor of 1.01 was used to avoid over dilution and masking of elemental releases due to the very low levels of release common to these ultra-durable LaBS glasses[5].

Table IV. Thermal history and processing characteristics of the six No RCRA - Sr melts.

<u>Melt</u>	<u>Temperature</u>	<u>Stirred</u>	<u>Thermal History</u>
1	1450° C	Yes (2, 3.3, 4.2)	Water Quenched
2	1450° C	Yes (2, 3.3, 4.2)	Water Quenched
3	1475° C	No	Water Quenched
4	1475° C	Yes (3.4)	Annealed (570° C)
5	1425° C	Yes (1.8, 2.6)	Air Quenched
6	1425° C	Yes (1.8, 2.6)	Annealed (570° C)

Results and Discussion

Glass Processing and Homogeneity

No Pb - Sr,Na

The initial No Pb - Sr,Na melt processed well at 1450° C with smooth stirring and appeared to be homogeneous during the stir (no large insoluble oxides). However, undissolved ThO₂ was detected by XRD after 3.7 and 4.5 hour stirs. Quantitative analysis indicated a reduction of ThO₂ with increased residence time. No undissolved ThO₂ was detected in the residue stir bar glass after 4.7 hours or in the quenched glass sample (after 5 hours). However, an opaque/opalescence material in the shape of a bowl, believed to be amorphous phase separation, formed on the top and extended down into the melt approximately 2-3 mm. It is believed that areas of relatively slow cooling caused this phase separation. The more quickly "quenched" bottom and sides (adjacent to the crucible immersed in water) of the melt were not opalescence. The slower rate of cooling at the center of the melt appears to have kinetically allowed the development of amorphous phase separation. This is believed to be caused by a combination of several factors. The introduction of sodium oxide into the glass coupled with an increase in boron relative to the base LaBS composition (12 to 18 mole percent) promotes phase separation. Amorphous phase separation is a common occurrence in some borosilicate glass compositions (i.e. Vycor®). Aluminum oxide is a known inhibitor of phase separation in alkali borosilicate glasses. Therefore, the dramatic decrease of aluminum oxide (24 to 14 mole percent) relative to the base LaBS glass composition could favor phase separation. However, the alumina levels known to inhibit phase separation in Vycor type glasses are in the range of 5 mole percent.

No RCRA - Na

Both No RCRA - Na melts were completely crystalline upon cooling and had a very high viscosity (i.e. manual stirring was difficult). The No RCRA - Na melt was not processable at 1450° C. It was very difficult to stir and the residual glass on the stir bar contained a significant amount of ThO₂. This melt was terminated after 3 hours. Compared to the 'No Pb - Sr,Na' melt, the 'No RCRA - Na' increases the Na₂O content (3.4 to 5.7 mole percent). This increases the Na atom content from 4.7 to 7.8 mole percent, which exceeds the total mole percent of Na, Sr and Ba of the 'No Pb - Sr,Na' melt (6.4 mole percent) of. This may be the overriding cause of the complete ceramic (crystalline) formation of this melt.

No Pb - Sr

The No Pb - Sr melt processed well at 1450° C. The No Pb - Sr melts stirred easily and were visually and XRD homogeneous after 3.5 hours at temperature. No phase separation was evident on cooling. The No Pb - Sr melt was deemed successful based on ability to process and homogeneity. All six of the stirs (glass on the stir bar) were homogeneous except for one. XRD identified quartz and cristobalite in the residual glass adhered to the stir bar of one of the two melts after 2.2 hours. This is believed to be an anomaly due to inadequate premixing rather than substandard processing. Undissolved SiO₂ would not be present due to a processing problem (i.e. solubility, inappropriate processing temperature, etc.). No phase separation occurred with the absence of Na₂O and an increase in Al₂O₃ (compared to No Pb - Sr,Na) given the same cooling schedule. The viscosity (while manually stirring) of this melt was comparable to 'No Pb - Sr,Na'. The absence of Na₂O and increased Al₂O₃ did not effect the viscosity.

No RCRA - Sr

Several No RCRA - Sr melts were processed with different thermal histories (Table IV). All six glasses were determined by XRD to be homogeneous. No phase separation was detected visually or by Transmission Electron Microscopy (TEM). Table IV summarizes processing characteristics of the six melts. The residual glass on both stir bars of melts #1 and #2 (1450° C, stirred, water quenched) was homogeneous. Two other glasses (melts #5 and #6) were melted at 1425° C. These were slightly more viscous with all but one of the stirrings homogeneous. After 1.8 hours, quartz was detected (by XRD) on the residual glass on the stir bar of one melt. Again, this is thought to be due to premixing, rather than processing. One of the 1425° C melts (melt #6) was used to evaluate the effect of slow cooling on the formation of amorphous phase separation. No evidence of phase separation was detected by visual observation or TEM.

Previous work has shown the base LaBS glass to successfully incorporate 15 elemental weight percent thorium into the glass after 5 hours during a static melt at 1475° C [6]. For comparison, No RCRA - Sr melts #3 and #4 were melted at 1475° C. Melt #3 was a static melt with a residence time of 3.4 hours with water cooling. Melt #4 was stirred three times and annealed. Both melts were homogeneous with no evidence of amorphous phase separation development. Table V gives the analyzed compositions of the three homogeneous glasses.

Table V. Analyzed compositions for the three homogeneous glasses (prior to PCT) in normalized weight percent oxide.

<u>Oxide</u>	<u>Base LaBS</u>	<u>No Pb - Sr</u>	<u>No RCRA - Sr</u>
SiO ₂	26.94	29.15	27.51
B ₂ O ₃	7.29	9.91	8.78
Al ₂ O ₃	22.54	19.06	20.37
SrO	---	0.56	1.35
PbO	8.04	---	---
BaO	1.99	0.03	---
ZrO ₂	0.93	0.86	0.95
La ₂ O ₃	5.25	8.49	8.58
Gd ₂ O ₃	10.90	11.68	11.45
Nd ₂ O ₃	2.97	3.78	3.81
ThO ₂	13.15	16.49	17.20

Durability

The (7-day) PCT results of the original LaBS, No Pb - Sr and No RCRA - Sr are summarized in Table VI. The normalized released rates for Si, B, Al Sr, and Ba are reported. No detectable quantities of Th or Gd (used as a neutron absorber) were detected in the PCT leachate. The pH values are also given. Although the pH values for these glasses are somewhat higher than previously reported[7], Na concentrations ranging from 0.5 to 8.0 ppm in the PCT leachate suggests a possible contamination problem. Two blanks were analyzed and were found to contain 0.23 ppm sodium. With no Na being introduced as part of these glasses, the sodium concentrations should not exceed the blanks. The Tekmar grinder used to crush the glass had been used previously for DWPF type glasses. This and repeated sieve use without proper cleaning may be the cause of sodium contamination in the PCT. Elevated Na levels may be the cause for an increase in pH. If the impurities (glass from previous PCT tests) contained significant amounts of alkali, these results could be skewed. The fact that sodium concentrations were detected in the leachates of these glasses, even though no sodium was added to the batch composition provides evidence supporting contamination. Future PCT's on the LaBS glasses will be conducted with new sieves to eliminate possible contamination during testing.

Table VI. Normalized release values of PCT results in percent.

<u>Element</u>	<u>Base LaBS</u>	<u>No Pb - Sr</u>	<u>No RCRA - Sr</u>
Si	0.05	0.017	0.0083
B	0.03	0.02	0.01
Al	0.02	0.02	0.005
Sr	---	0.0075	0.015
Ba	0.015	---	---
pH	9.78	8.71	8.08

All other components were below detectable limits.

Conclusions

The lanthanide borosilicate glass composition, being evaluated by SRTC for plutonium disposition as part of the Fissile Material Disposition program, has been processed with greater than 15 elemental weight percent thorium (a plutonium surrogate) without the presence of lead oxide and barium oxide in the glass. The glass composition is a result of continuing compositional development to replace the lead with strontium and/or sodium. Two homogeneous lead free melts have been processed. The first (No Pb - Sr) one replaced one-fifth of the total lead with Sr on a mole percent basis. Other changes included slightly less aluminum with increased boron and silica contents. The second glass composition (No RCRA - Sr) was identical to the first (No Pb - Sr) with an additional 1:1 replacement of barium with strontium on a mole percent basis.

PCT results show the no RCRA glass (No RCRA - Sr) to be more durable than the original LaBS glass (with lead) with similar Th loadings. Elevated Na levels in the PCT leachate of glasses compared to blanks (no glass) indicate probable contamination from unclean sieves or grinders. pH values and normalized elemental releases of PCT leachates are slightly higher than previously reported for similar glasses. This may be due to alkali containing glasses from previous PCT's being introduced into this PCT through contamination. Alkali elements, as they leach out of glass, increase pH, subsequently causing increased leaching.

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