Liquidus temperature and chemical durability of selected glasses to immobilize rare earth oxides waste

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Abstract

Pyroprocessing is a reprocessing method for managing and reusing used nuclear fuel (UNF) by dissolving it in an electrorefiner with a molten alkali or alkaline earth chloride salt mixture while avoiding wet reprocessing. Pyroprocessing UNF with a LiCl-KCl eutectic salt releases the fission products from the fuel and generates a variety of metallic and salt-based species, including rare earth (RE) chlorides. If the RE-chlorides are converted to oxides, borosilicate glass is a prime candidate for their immobilization because of its durability and ability to dissolve almost any RE waste component into the matrix at high loadings. Crystallization that occurs in waste glasses as the waste loading increases may complicate glass processing and affect the product quality. This work compares three types of borosilicate glasses in terms of liquidus temperature (T_L): the International Simple Glass designed by the International Working Group, sodium borosilicate glass developed by Korea Hydro and Nuclear Power, and the lanthanide aluminoborosilicate (LABS) glass established in the United States. The LABS glass allows the highest waste loadings (over 50 mass% RE_2O_3) while possessing an acceptable chemical durability.

Keywords: liquidus temperature, durability, rare earth waste glass, crystallization

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1. Introduction

1.1 Rare earth oxides in pyroprocessing

To meet energy requirements, the Republic of Korea is planning to construct six nuclear power plants (NPPs) in addition to the five NPPs under construction and 23 NPPs in operation as of December 2012 [1]. However, the accumulated used nuclear fuel (UNF) will reach the maximum capacity of temporary storage facilities by 2016. This major issue of managing UNF and space requirement needs to be resolved for next-generation safety [2]. One alternative for managing the UNF is using reprocessing technology to reduce the amount of high level waste (HLW) volume in the repository site prior to disposal [2,3]. Unlike wet reprocessing technology, such as the plutonium and uranium extraction process, molten salt reprocessing technology, such as pyroprocessing, minimizes the proliferation risk [2] and produces less liquid waste.

Pyroprocessing separates transuranic elements by electrolytic reduction, including uranium from UNF, for reuse as fuel in fast reactors [3,4]. The waste contains rare earth (RE) fission products that are converted to chlorides in the electrolyzer [3-5]. Once these fission products become too concentrated in the electrolyzer, the separations efficiency is negatively impacted. Thus, at that stage, the fission products either need to be selectively removed or the salt must be replaced.

One method to selectively separate the RE chlorides from the salt is oxygen sparging to convert these species to oxides or oxychlorides that precipitate from the salt melt [6]. Converting RECl_3 into REOCl and REOCl to RE_2O_3 in the presence of oxide ions proceeds according to the following reactions:

According to the literature [6-9], full conversion of the REs to oxides in the LiCl-KCl eutectic salt melt is difficult. According to Cho et al. [7] and Hayashi and Minato [8], some RE^{3+} cations tend to remain in the form of stable oxychlorides. Katayama et al. [9] and Suh et al. [10,11] reported that the stability of RE_2O_3 and REOCl , while related to the oxide-ion activity ($p\text{O}^{2-}$), is higher for some REs (e.g., Ln^{3+}) than for others (e.g., Gd^{3+}).

Provided that a pure stream of RE oxides can be generated, a borosilicate glass is a desirable waste form from a standpoint of waste loading potential and chemical durability [12,13].

1.2 Rare earth oxides in borosilicate glasses

Borosilicate glass has been selected for HLW immobilization because it 1) has a high tolerance for the chemical complexity of the wastes, 2) has excellent chemical durability, 3) melts easily, and can accommodate high waste loadings [14,15]. In this work, we compare three types of borosilicate glasses all of which have been established as possible candidates for the vitrification of nuclear wastes. Our focus is to compare their crystallization behavior, in particular the liquidus temperature (T_L) and the equilibrium crystallinity below the T_L . These three types of borosilicate glasses are the International Simple Glass (ISG) designed by the International Working Group, sodium borosilicate glass developed by Korea Hydro and Nuclear Power, and the lanthanide aluminoborosilicate (LABS) glass established in the United States.

The ISG was designed as a reference benchmark HLW glass for dissolution studies [16]. Various versions of ISG with lower boron content were used for structural studies [14,15,17]. Their glasses can accommodate up to 30 mass% of waste loadings and can be processed at 1300 to 1400°C. Glasses containing SiO₂, B₂O₃, Na₂O, and Li₂O, formulated by Korea Hydro and Nuclear Power in feasibility studies of lanthanide waste [18], accommodated 20 to 40 mass% of waste oxides when melted at 1200 to 1300°C. Finally, LABS glass with SiO₂:B₂O₃:Al₂O₃ in the ratio 3:1:2 by mass, respectively, allowed the RE loadings of up to 62 mass% when melted at 1300 to 1450°C [12,13,19,20].

In Korea, the cold crucible induction melter (CCIM) was designed by the Nuclear Environment Technology Institute to vitrify low- and intermediate- level radioactive waste [21]. Unlike joule-heated melters for which the operating temperature is limited to 1150°C, the CCIM can be operated at temperatures up to 1700°C. This high temperature capability allows for processing of nuclear waste glasses with high liquidus temperatures (T_L). The CCIM may be a viable option for some of the glasses processed in this study.

Glasses with high waste loading can potentially contain a large fraction of components that form crystalline phases [22]. Crystallization can be problematic if large, high-density crystals precipitate and settle in the melter [22]. In the demonstration test of the CCIM at Savannah River National Laboratory for vitrification of a simulated HLW, researchers concluded that crystal settling might interfere with, and potentially obstruct, the bottom discharge valve of the melter [21]. In addition, RE oxides have a strong tendency to form crystalline phases in glass melts [23] depending on the type, size, and quantity of the crystal [17]. Fortunately, small crystals and crystals with densities close to that of the melt settle slowly and can be completely removed from the melter to the canister.

While in the canister, crystals continue to grow during cooling. Generally, RE-containing glasses possess high chemical durability [18-20,23-25]. However, if the crystalline phases remove important

glass network components from the matrix glass, crystallization can compromise the chemical durability of the residual glass.

Rare earth oxides, such as Gd_2O_3 and La_2O_3 , were proposed as nonradioactive surrogates for actinides to immobilize actinide-bearing radioactive wastes. According to Li et al. [23], changing the $\text{Na}_2\text{O}/(\text{Al}_2\text{O}_3+\text{Na}_2\text{O})$ ratio in the baseline glass composition will effects REs solution behavior in the glass. Zhao et al. [24] made a high-durability borosilicate glass-ceramic containing Gd as a surrogate for actinides that formed a cation-oxyapatite crystalline phase.

Rare earth silicates precipitate from glasses in various morphologies, such as needle-, plate-, and rod-like crystals [19]. Quintas et al. [14-17], Ahn et al. [26], and Crum et al. [27-28] detected crystals with an apatite structure, such as oxyapatite or more specifically $\text{Ca}_2\text{RE}_8\text{Si}_6\text{O}_{26}$, which formed during thermal treatment of the glasses. Quintas et al. [14] determined that a small fraction of $\text{Ca}_{2+x}\text{Nd}_{8-x}(\text{SiO}_4)_6\text{O}_{2-0.5x}$ ($x=0.14$ to 0.41) phase formed in a complex waste glass with a significant amount of CaO and RE_2O_3 . Peeler et al. [19] reported RE silicates found as $\text{RE}_3\text{BSi}_2\text{O}_{10}$ crystals in LABS-Sr glass.

Quintas et al. [17] showed that lanthanides beyond Eu have a low crystallization tendency and argued that RE elements with smaller ionic radii (e.g., Ce =101 pm, Pr =99 pm, Nd = 98.3 pm) tend to crystallize, whereas La (103.2 pm) has a slight tendency to form crystals even though it has a small ionic radius [29]. Also, RE ions with ionic radii close to Ca^{2+} (100 pm), such as Pr and Nd, are likely to be present in the apatite crystalline phase. Bondar [30] and Crum et al. [28] were able to substitute Y_2O_3 and a wide variety of RE_2O_3 into the oxyapatite structure.

1.3 Solubility of rare earth oxides and liquidus temperature

Suppose a single RE oxide is added in an increasing fraction of glass of a given composition at a given temperature until a crystalline phase begins to precipitate at equilibrium. The corresponding RE oxide fraction represents its solubility and the corresponding temperature is the T_L of the glass in which the RE oxide is at the solubility limit. Solubility of a RE is a function of glass composition and temperature. As Caurant et al. [32] demonstrated, the solubility of RE cations depends on their valence states where RE(IV) are less soluble than RE(III). Kim and Lee [18] formulated an $\text{SiO}_2 - \text{B}_2\text{O}_3 - \text{Na}_2\text{O} - \text{Li}_2\text{O} - \text{RE(III)}_2\text{O}_3/\text{RE(IV)}\text{O}_2$ glass where RE(III) = Nd, La, Eu, Gd, Sm, Y and RE(IV) = Ce, Pr. For these glasses, T_L is $<950^\circ\text{C}$ even when the RE fraction was as high as 20 mass% RE oxides.

The major focus of this study was to collect information about the formation of crystalline phases from glasses containing high fractions of RE oxides. This preliminary research compares three different glass compositions for feasibility of immobilizing rare earth oxide waste streams from

pyroprocessing. In this work, the product consistency test (PCT) was performed for selected crystal-free glasses to compare the three types of compositions tested. No attempt was made at this stage to determine the impact of crystallization in these glasses on their chemical durability. The crystallinity of glasses produced in the melter and poured into the canister are unlikely to reach equilibrium crystallinity because the rate of crystallization is generally not rapid enough.

2. Experimental Methods

Two experimental steps were performed for this study: 1) glass fabrication and 2) heat treatment of glass samples to determine liquidus temperatures [33]. The techniques used were optical microscopy, scanning electron microscopy with energy dispersive spectroscopy (SEM-EDS), and X-ray diffraction (XRD) with whole pattern fitting. Chemical durability was assessed using the PCT [35] as an indicator for the waste form acceptability. The experimental steps and the analytical techniques are described below.

2.1 Glass fabrication

The 250-g batches of ISG glasses (FL and FR), candidate glasses (CG), and LABS glass (see Table 1) were made from fine powders of oxides (SiO_2 , ZrO_2 , Al_2O_3 , La_2O_3 , CeO_2 , Nd_2O_3 , Eu_2O_3 , Gd_2O_3 , Pr_6O_{11} , Sm_2O_3 , and Y_2O_3), carbonates (Na_2CO_3 , CaCO_3 , and Li_2CO_3), and boric acid. The batches were homogenized in an agate vibratory mill for 4 min. Batches were melted in a covered Pt/10%Rh crucible at 1300°C for 1 h except the LABS glass, which was melted at 1325°C (Table 1). The melts were poured on an Inconel[®] plate to air quench. The cooled glasses were ground in a tungsten carbide mill for 4 min, remelted for 1 h, and then quenched under the same conditions. Glass melting temperatures were purposely selected within the range of 1300 to 1400°C to facilitate processing. All glasses were observed through the optical microscope for any phase separation or crystallization before testing. The ISG and CG glasses were homogeneous and transparent, while the LABS glass appeared transparent in transmitted light and had a dark auburn color. No attempt was made to measure the glass compositions after melting because all of the glasses were batched using analytical grade chemicals and melted in covered Pt crucibles. In addition, very little volatility was observed suggesting no preferential loss of volatile components during melting.

Four ISG-based glasses were prepared. Two contained only La_2O_3 as a typical RE element (FL glasses) and the other two (FR glasses) contained the full spectrum of anticipated pyroprocessing RE composition (in mass%) 38.45 Nd_2O_3 – 23.76 CeO_2 – 11.62 La_2O_3 – 11.14 PrO_2 – 7.68 Sm_2O_3 – 4.86 Y_2O_3 – 1.46 Eu_2O_3 – 1.02 Gd_2O_3 . The two FL glasses were prepared to compare with FR glasses by representing only one RE oxide in the waste composition. We tested two levels of waste loading: 10 and 15 mass%.

In addition, two borosilicate compositions (designated CG glasses in Table 1) were prepared based on a study by Kim and Lee [18], who recommended them for their high waste loading and low T_L . Glasses fabricated with 20 and 25 mass% waste, consisting of a mixture of 38.20 mass% Nd_2O_3 , and 61.80 mass% CeO_2 normalized to the ratio of original composition in the waste spectrum were melted at 1300°C. Finally, a LABS glass was made with 53 mass% of the 38.20 Nd_2O_3 – 61.80 CeO_2 (in mass%) mixture (the same as CG glasses). In these CG and LABS glasses, the waste composition was represented by Nd_2O_3 and CeO_2 because of their high composition in the anticipated pyroprocessing waste.

2.2 Liquidus temperature

The T_L of each glass was measured following ASTM C1720-11, specifically, the crystal fraction extrapolation method [33,34]. The glass was crushed and sieved to the particle size recommended in the procedure, between 0.422 mm and 4 mm (+40/-5 mesh). The sieved glasses were ultrasonically washed three times in a clean glass beaker using deionized water. The glass particles then were submerged in ethanol and ultrasonically cleaned three times. After decanting the ethanol, the samples were dried in an open glass beaker at $\geq 90^\circ\text{C}$ for ≥ 1 h in an oven. The glasses were retrieved and stored in clean containers prior to use.

The furnace for heat treatment was calibrated using glass of known T_L (SRM-773) to determine the uncertainty of the thermocouple and furnace used during the test. All glass samples were heat treated in a covered 1.2-cm³ Pt/10%Rh crucible at temperatures from 850°C to 1150°C in increments of 50°C, or less if necessary. The samples were heat treated for 24 ± 2 h at temperatures $> 900^\circ\text{C}$ and for up to 48 ± 4 h at temperatures $< 900^\circ\text{C}$.

After each heat treatment, the samples were air quenched and divided into two portions for analysis. One portion was crushed for XRD analysis in a tungsten carbide mill to a fine powder with a known amount of CaF_2 as an internal standard.

2.3 X-ray diffraction

The powdered samples were doped with 5 mass% CaF_2 and analyzed with XRD using a Bruker® D8 Advance (Bruker AXS Inc., Madison, WI) XRD with Cu K_α emission and a LynxEye™ position-sensitive detector with a collection window of $3^\circ 2\theta$. Scan parameters were 5 to $70^\circ 2\theta$ with a step of $0.015^\circ 2\theta$ and a 0.3-s dwell at each step. Crystalline phase identification was done with DIFFRAC^{plus} EVA (Bruker AXS). Further analysis was done using TOPAS 4.2 (Bruker AXS) whole pattern fitting software. The added CaF_2 functioned as an internal standard for quantification of the other crystalline phases in the sample. Once the crystal fractions were determined, the T_L was calculated using the ASTM C1720-11 procedure [33,34].

2.4 Microscopy

The other portion of the T_L sample was selected for optical microscopy and SEM-EDS to determine crystal morphology and chemical composition. Optical microscopy was performed with an Olympus SZH10 (Waltham, MA). The SEM-EDS analysis was conducted with a JSM-7001F field-emission gun microscope (JEOL USA, Inc. Peabody, MA) coupled with a Bruker xFlash 6|60 EDS detector. The samples were prepared in thin sections with specimens ~0.25 mm thick. The thin sections were polished to a 1- μ m finish.

2.5 Chemical durability study

The samples for durability testing were prepared and measured using the PCT designated as ASTM C1285-14 [35]. Based on the procedure, the glasses were sieved to the particle size of -100/+200 mesh (i.e., 74 to 149 μ m). The glasses were crushed in a tungsten carbide vibratory mill and sieved to achieve the recommended size. The sieved glasses were ultrasonically washed with deionized water three times. Then, the deionized water was replaced with absolute ethanol, and the material was washed again three times. The samples were then dried in the oven overnight at $90\pm 10^\circ\text{C}$. The glasses were retrieved and placed into Teflon vessels filled with deionized water for a recommended ratio volume of solution to mass of solid ($V_{\text{soln}}/m_{\text{solid}}$) of 10 ± 0.5 mL. Each glass was tested by PCT in duplicate. Blanks also were prepared with deionized water at a leachant volume similar to that of the sample. All samples and blanks were placed together in a forced air convection oven at $90\pm 2^\circ\text{C}$ for 7 d.

After the 7-d leaching period, the samples were retrieved and cooled to room temperature. The leachates were removed from the vessels, pH was measured and recorded, and remaining solutions were filtered with a 0.45- μ m syringe filter and stored in a clean container. Nitric acid (1% from the leachate volume) was spiked into the filtered leachate prior to analysis to prevent possible hydrolysis of heavy cations. The solutions were analyzed using inductively coupled plasma-optical emission spectroscopy for glass components and inductively coupled plasma-mass spectroscopy was used for RE components. Normalized releases of elements were then calculated using ASTM C1285-14 [35].

3. Results and Discussions

3.1 Liquidus temperature

We obtained the T_L as an intercept of the trendline fitted to crystal fraction data (obtained by XRD and the TOPAS refinement software) against heat treatment temperature as shown in Fig. 1. For FL10 and FL15 glasses, the T_L values were 966°C and 1052°C , respectively, and 970°C and 1052°C for FR10 and FR15 glasses, respectively. Two outliers were omitted because they clearly did not agree with the other points from FL10 at 849° and 904°C , and outliers at 880°C and 904°C were omitted in

FL15 and FR15 plots. At equal waste loadings, T_L values of FL and FR were close to each other with relative standard deviations of 0.26% and 0.02% for 10 and 15 mass% waste loadings, respectively. This indicates the La_2O_3 alone can represent the full spectrum of RE components when it comes to the crystallinity.

Previous studies showed that B(IV)/B(III) ratio decreased with increasing RE ionic radius and increasing Ln concentration in the glass composition [15,17]. However, the boron content in the glass composition in those studies was two times lower than those used in this study. In slow-cooled, low-boron glasses, a La-containing glass had a lower crystallization tendency than in glasses containing RE with smaller ionic radii than Eu [17]. This may explain the tendency of boron to form LaBSiO_5 (detected as CeBSiO_5) in FL glasses while staying in glass network in FR glasses containing mixed REs. Fig. 2 shows XRD diagrams of crystalline phases detected in the samples.

In spite of having similar T_L values, the FL and FR glasses formed different primary crystalline phases distinguished by XRD (see Fig. 2); FL glasses precipitated LaBSiO_5 crystals, which were detected as CeBSiO_5 (FL glasses contained La_2O_3 as a single lanthanide) and FR glasses precipitated oxyapatite in the form of $\text{Ca}_2\text{RE}_8\text{Si}_6\text{O}_{26}$. Fig. 3 shows a micrograph of a 15 mass% waste-loaded FR glass with needle-like crystals and hexagonal platelets with a central hole, which probably is a tiny bubble on which the crystal nucleated. Oxyapatite can likely accommodate any RE element [14,17,26-28] and even Na and Li [17], or Na, Sr and Cs [28]; however, Kim and Lee [18] did not find any Li in Nd-silicate crystals that precipitated from a Li-containing borosilicate glass. Boron substitution in the Si sites in the apatite structure was reported by Quintas et al. [17], Ahn et al. [26], and Crum et al. [28].

Kim and Lee [18] selected two candidate glasses with high waste loadings that were crystal-free at $\sim 1300^\circ\text{C}$. We reproduced their compositions except we used only two major RE components, CeO_2 and Nd_2O_3 (designated CG glasses in Table 1) in lieu of their full RE mix. Fig. 1 shows crystallinity in CG glasses as function of temperature with data fitted by linear trendlines, omitting outliers at 1042°C and 1075°C due to inconsistencies with other points. XRD analysis identified CeO_2 in CG glasses as showed in Fig. 2, pictured by SEM in Fig. 4 from heat-treated sample of CG20 at 999°C for 23.8 h. From EDS results, we determined that the cubic crystals contained >70 mass% CeO_2 . The crystals also contained ~ 4 mass% Nd_2O_3 and large fractions of Na_2O and SiO_2 , probably from the surrounding glass matrix.

The T_L values were 1080°C and 1118°C for CG20 and CG25, respectively. In contrast, Kim and Lee [18] reported $T_L < 950^\circ\text{C}$ in the glass containing the full spectrum of RE with the primary phase of Nd-silicate. Even though glasses in the present work contained a mixture of only two REs oxides, Nd_2O_3 and CeO_2 , one would expect that the oxide with a higher oxidation state, CeO_2 , would

precipitate preferably to that of a lower oxidation state, Nd_2O_3 , which would remain dissolved. As Kim and Lee [18] admit, their melts were probably affected by the material dissolved from clay crucibles in which they made the glasses (they switched to using Pt crucibles for heat treatments).

For the LABS glass, the heat treatment was carried out in duplicate. Fig. 1 shows the primary crystalline fraction in the LABS glass as a function of temperature, yielding $T_L = 1201^\circ\text{C}$. Fractions of crystalline phases detected by XRD are summarized in Table 2 and the distinguished peaks are shown in Fig. 2. The uncertainties of T_L results were contributed from furnace error bars of $\pm 3^\circ\text{C}$ and ± 0.005 for crystal fraction extrapolation (added to Fig. 1) to account for estimated errors associated with the technique. Unlike ISG and CG glasses, LABS glass produced four kinds of crystalline phases during heat treatment.

Fig. 5 shows the crystal morphology in the LABS glass heat-treated at 999°C for 23.7 h. The primary crystalline phase, the light gray crystals in the figure, are Ce-borosilicate $[\text{Ce}_3(\text{BSiO}_6)(\text{SiO}_4)]$, the same as reported for LABS glass containing Sr [19]. The other three crystalline phases observed were small white cubic crystals of CeO_2 that occasionally formed chains, black crystals of mullite ($\text{Al}_5\text{SiO}_{9.5}$), and corundum (Al_2O_3) crystals. This glass showed higher tendency of Ce^{3+} than Ce^{4+} crystallization, probably enhanced and substituted by Nd^{3+} in crystal structure due to similar ionic radii.

Even though boron content was low in this glass, it had a tendency to precipitate the primary crystalline phase with a low oxidation Ce^{3+} . The high oxidation Ce^{4+} probably crystallized as CeO_2 during cooling after the heat treatment because the crystal fractions were present in all samples regardless of the heat treatment temperatures in a range of 1.41 to 1.95 mass%. Crum et al. [28] also observed CeO_2 crystals with ZrO_2 in the glass-ceramic for mixed waste. The mullite fraction seems to follow a primary phase trend. No mullite was detected above 1097°C , whereas corundum formed above 1147°C (at 1147°C , corundum only appeared in one of the duplicates).

The T_L may limit the waste loading in glass. Suppose we compare FL15 or FR15 with CG25 and LABS glasses, the latter glass shows a higher T_L . The lower T_L of CG glass is caused by a high content of alkalis and the higher T_L of alkali-free LABS glass is associated with its high content of REs.

3.2 Product consistency tests

Table 3 summarizes the normalized elemental releases (in g/m^2) of glass components from quenched crystal-free samples. Uncertainties were calculated based on the averages from duplicate samples. Releases of B and Na from ISG and LABS glasses were far lower (0.03 to 0.46 g/m^2 and 0.47 to 0.53 g/m^2 , respectively) than those from the standard environmental-assessment glass (5.36 to

8.35 and 4.28 to 7.61 g/m² for B and Na, respectively) [12,13,19], the CG glasses (36.91 to 46.71 g/m² and 30.42 to 40.10 g/m² for B and Na, respectively), and the glass-ceramic waste form (27.8 and 23.7 g/m² for B and Na, respectively) reported by Kim and Heo [31]. As Table 3 shows, the PCT normalized releases of CG glasses were even higher than those from environmental-assessment glass. This finding is consistent with the extremely high Na₂O content in these glasses that is not compensated by the charge-balancing Al₂O₃ [36]. On the other hand, the PCT B, Si, and Al releases from the LABS glass were within the range of previous studies (0.003 to 0.041 B g/m², 0.002 to 0.013 Si g/m², and 0 to 0.013 Al g/m²) [12,13,19].

All glasses show extremely low releases of RE components as shown in Table 3: $\sim 10^{-4}$ g/m² from ISG and LABS glasses and $\sim 10^{-3}$ g/m² from CG glass. The detection limit was less than 0.25 and 0.24 µg/L for Ce and Nd, respectively, in the solution. The FL15 and FR15 glasses exhibited similar results for all components even though the FL15 only had one RE component (La₂O₃).

4. Conclusion

Three different glass types (ISG, alkali-borosilicate glass, and LABS glass) designed to immobilize lanthanide waste from used-fuel pyroprocessing were tested for crystallinity and chemical durability. Differences in the T_L and PCT between ISG glasses with the full set of RE components (FR glasses) and with only La₂O₃ (FL glasses) appeared insignificant. The durability of the alkali-borosilicate glass containing over 23 mass% Na₂O was found to be insufficient. The LABS glass had the highest T_L (1201°C) and waste loading (53 mass%) and exhibited superior durability.

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Figure Captions:

Fig. 1. Crystal fraction as a function of temperature for FL, FR, CG, and LABS glasses.

Measurements were made in duplicate. Error bars on points are $\pm 3^{\circ}\text{C}$ for temperature and ± 0.005 for the crystal fraction.

Fig. 2. XRD diagram of each crystalline phase

Fig. 3. Morphology of oxyapatite $[\text{Ca}_2\text{RE}_8\text{Si}_6\text{O}_{26}]$ crystals in heat-treated FR glass (FR15 at 980°C for 25.6 h)

Fig. 3. Morphology of CeO_2 crystal in heat-treated CG glasses (CG20 at 999°C for 23.8 h)

Fig. 4. Morphology of all crystals in heat-treated LABS glass (999°C for 23.7 h)

Table Captions:

Table 1. Glass melting temperatures (T_M), compositions (in mass fraction), and waste loading

Table 2. Fraction of crystalline phases in LABS glass by XRD in mass fractions

Table 3. Summary of 7-day PCT normalized releases (g/m^2) from crystal-free glasses

Figures and Tables

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Fig. 5. Morphology of all crystals in heat-treated LABS glass (999°C for 23.7 h)

Table 1. Glass melting temperatures (T_M), compositions (in mass fraction), and waste loading

Oxides	FL10	FL15	FR10	FR15	CG20	CG25	LABS
T_M (°C)	1300	1300	1300	1300	1300	1300	1325
Al ₂ O ₃	0.0542	0.0512	0.0542	0.0512	-	-	0.1930
B ₂ O ₃	0.1560	0.1473	0.1560	0.1473	0.1143	0.1071	0.0797
CaO	0.0448	0.0423	0.0448	0.0423	-	-	-
Li ₂ O	-	-	-	-	0.0343	0.0321	-
Na ₂ O	0.1093	0.1033	0.1093	0.1033	0.2514	0.2357	-
SiO ₂	0.5064	0.4782	0.5064	0.4783	0.4000	0.3751	0.1973
ZrO ₂	0.0293	0.0277	0.0293	0.0277	-	-	-
CeO ₂	-	-	0.0238	0.0357	0.0764	0.0955	0.2024
Eu ₂ O ₃	-	-	0.0015	0.0022	-	-	-
Gd ₂ O ₃	-	-	0.0010	0.0015	-	-	-
La ₂ O ₃	0.1000	0.1500	0.0116	0.0174	-	-	-
Nd ₂ O ₃	-	-	0.0384	0.0577	0.1236	0.1545	0.3276
PrO ₂	-	-	0.0111	0.0167	-	-	-
Sm ₂ O ₃	-	-	0.0077	0.0115	-	-	-
Y ₂ O ₃	-	-	0.0049	0.0073	-	-	-
Sum	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
Waste loading (mass%)	10	15	10	15	20	25	53

Table 2. Fraction of crystalline phases in LABS glass by XRD in mass fractions

Temp (°C)	CeO ₂	Ce-borosilicate	Mullite	Corundum
999	0.0179	0.2887	0.1633	-
1050	0.0187	0.2380	0.1241	-
1097	0.0184	0.1730	0.1027	-
1147	0.0190	0.0709	-	0.0130
1202	0.0143	-	-	0.0229

Table 3. Summary of 7-day PCT normalized releases (g/m²) from crystal-free glasses

Element/Glass	FL15	FR15	CG20	CG25	LABS
B	0.46±0.02	0.42±0.06	46.71±0.43	36.91±0.11	0.03±0.002
Si	0.16±0.001	0.14±0.03	19.67±0.44	10.53±0.007	0.01±0.001
Al	4.9±0.3×10 ⁻³	5.8±1.1×10 ⁻³	-	-	0.3±0.4
Ca	0.04±0.002	0.03±0.004	-	-	-
Li	-	-	27.72±0.02	20.25±0.2	-
Na	0.53±0.001	0.47±0.07	40.10±1.13	30.42±0.90	-
Ce	-	ND	1.6±0.7×10 ⁻³	3.2±0.3×10 ⁻⁴	1.9±1.3×10 ⁻⁵
Nd	-	ND	1.9±2.2×10 ⁻³	1.9±0.6×10 ⁻³	1.3±0.4×10 ⁻⁴
La	6.0±0.9×10 ⁻⁵	6.3±2.3×10 ⁻⁵	-	-	-
Eu	-	8.8±3.2×10 ⁻⁵	-	-	-
Pr	-	8.3±3.0×10 ⁻⁵	-	-	-
Sm	-	9.0±3.5×10 ⁻⁵	-	-	-
Y	-	8.2±2.9×10 ⁻⁵	-	-	-
ND: The value was below limit of detection.					