

## The Effect of Glass Composition Containing RE Oxide Waste Glass on Liquidus Temperature

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### ABSTRACT

The liquidus temperature ( $T_L$ ) of rare earth (RE) was determined for aluminoborosilicate glasses for treating americium and curium that have been studied previously. Their work covers a wide range of glass composition with various crystalline phases as primary phase. Present work is aimed at understanding the effect of glass composition on  $T_L$  for waste glasses designed for vitrifying RE oxides wastes. In a sufficiently narrow composition region, this effect can be represented by a first-order model fitted measured  $T_L$  versus composition data. Test glasses were formulated by varying of component fractions one-at-a-time. The glasses contained  $\text{SiO}_2$ ,  $\text{B}_2\text{O}_3$ , and  $\text{Al}_2\text{O}_3$  as glass formers and  $\text{Nd}_2\text{O}_3$  with  $\text{CeO}_2$  as simulated RE waste. Twenty glasses were made to investigate crystallization as a function of temperature and glass composition. The primary crystalline phase was Ce-borosilicate ( $\text{Ce}_3\text{BSi}_2\text{O}_{10}$ ), secondary phases were Al-containing crystals ( $\text{Al}_2\text{O}_3$  and  $\text{Al}_{10}\text{Si}_2\text{O}_{19}$ ), and crystalline  $\text{CeO}_2$ . A first-order model was fitted to crystal fraction versus glass composition data. Generally,  $\text{SiO}_2$  and  $\text{B}_2\text{O}_3$  tend to suppress crystallization,  $\text{Al}_2\text{O}_3$  has little effect, and, as expected, RE components ( $\text{Nd}_2\text{O}_3$  and  $\text{CeO}_2$ ) promote it. The correlation coefficient,  $R^2$ , was 0.89 for the primary crystalline phase  $T_L$  as a linear function of composition.

### INTRODUCTION

Rare earth aluminoborosilicate (LABS) glasses have been developed for treating Am and Cm in the Savannah River Site's (SRS) F-Canyon [1,2]. Based on excellent waste loading of these glasses for over 40 mass%, a similar glass composition was adapted to accommodate the lanthanide oxides  $\text{CeO}_2$  and  $\text{Nd}_2\text{O}_3$ . These lanthanides were representative for mixed lanthanides waste stream that will be generated from reprocessing of spent nuclear fuel using pyroprocess technology. This technology has been tested in pilot scale study since 2012 in Korean Atomic Energy Research Institute (KAERI) [3]. We formulated and produced 20 glass compositions by modifying the baseline glass composition of 19.73  $\text{SiO}_2$  – 7.97  $\text{B}_2\text{O}_3$  – 19.30  $\text{Al}_2\text{O}_3$  – 20.24  $\text{CeO}_2$  – 32.76  $\text{Nd}_2\text{O}_3$  in mass%. The waste loading ranged from 49.5 to 56.5 mass%. The components varied one at a time while keeping remaining components in equal proportions. A similar approach has been used before to study the component effects on spinel crystals [4]. In this paper, we discussed the effects of composition of these glasses on crystal fractions and the liquidus temperature ( $T_L$ ).

## EXPERIMENTAL DETAILS

Twenty glasses were fabricated by mixing boric acid and oxides of silicon, aluminum, and rare earth elements. The batches were mixed in the agate mill and melted in covered Pt/Rh crucibles for 1 hour. The melting temperature ranged from 1325 to 1475°C. The melts were poured on a steel plate and air quenched. The glasses were ground in the tungsten carbide mill and remelted at similar conditions to assure homogeneity. The glass compositions are listed in Table I with both melting temperature ( $T_m$ ) and waste loading as sum of CeO<sub>2</sub> and Nd<sub>2</sub>O<sub>3</sub> content (in mass%).

**Table I.** Glass compositions in mass%, melting temperature ( $T_m$ ), and waste loading (in mass%)

Glass	SiO <sub>2</sub>	B <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	CeO <sub>2</sub>	Nd <sub>2</sub> O <sub>3</sub>	Sum	$T_m$ (°C)	Waste loading
HS5	24.73	7.47	18.10	18.98	30.72	100	1325	49.7
HS3	22.73	7.67	18.58	19.49	31.53	100	1325	51.0
LS3	16.73	8.26	20.02	21.00	33.98	100	1325	55.0
LS5	14.73	8.46	20.51	21.50	34.80	100	1350	56.3
HB5	18.66	12.97	18.25	19.14	30.98	100	1350	50.1
HB3	19.09	10.97	18.67	19.58	31.69	100	1350	51.3
LB3	20.37	4.97	19.93	20.90	33.82	100	1365	54.7
LB5	20.80	2.97	20.35	21.34	34.53	100	1385	55.9
HA5	18.51	7.47	24.30	18.99	30.73	100	1475	49.7
HA3	19.00	7.67	22.30	19.49	31.54	100	1425	51.0
LA3	20.46	8.26	16.30	21.00	33.98	100	1365	55.0
LA5	20.95	8.46	14.30	21.50	34.79	100	1375	56.3
HC5	18.49	7.47	18.09	25.24	30.70	100	1375	55.9
HC3	18.99	7.67	18.58	23.24	31.53	100	1375	54.8
LC3	20.47	8.27	20.03	17.24	33.99	100	1375	51.2
LC5	20.97	8.47	20.51	15.24	34.81	100	1400	50.1
HN5	18.26	7.37	17.87	18.74	37.76	100	1375	56.5
HN3	18.85	7.61	18.44	19.34	35.76	100	1375	55.1
LN3	20.61	8.32	20.16	21.15	29.76	100	1375	50.9
LN5	21.20	8.56	20.74	21.75	27.76	100	1385	49.5

Liquidus temperature was measured following the ASTM C1720-11 procedure, specifically the crystal fraction extrapolation method [5,6]. Selected samples were heat-treated in duplicate for reproducibility. After heat-treatments to various temperatures range of 900-1200°C, portions of air-quenched samples were crushed in the tungsten carbide mill to a fine powder. A known amount of CaF<sub>2</sub> was added to each sample as an internal standard. The samples were analyzed with a Bruker® D8 Advance (Bruker AXS Inc., Madison, WI) x-ray diffractometer (XRD) and crystalline phases were identified using the DIFFRAC<sup>plus</sup> EVA (Bruker AXS) and quantified with whole pattern fitting TOPAS 4.2 (Bruker AXS) software.

## RESULTS AND DISCUSSION

The  $T_L$  is the maximum temperature at which the primary crystalline phase is at equilibrium with the melt. If a single RE crystalline form exists in equilibrium with a RE-containing molten glass at a certain temperature below  $T_L$ , the temperature at which the original glass was equilibrated equals the  $T_L$  of the matrix glass. For a reasonably small composition region, we can model the  $T_L$  as a linear function of composition using the relationship [1,2,4]

$$T_L = \sum_{i=1}^N T_{Li} g_i \quad (1)$$

where  $T_{Li}$  is the  $i$ -th component coefficient,  $N$  is the number of components in the model, and  $g_i$  is the mass fraction of the  $i$ -th component. The  $T_L$  in Equation 1 is the true  $T_L$  only for the primary crystallization phase.

Accordingly, when the crystal fraction,  $c$ , versus  $T$  data for which the  $T$  is sufficiently close to  $T_L$  to allow linear fitting, one can represent the  $c$  versus  $T$  data set with the relationship  $c = \sum_{i=1}^N b_i g_i (\sum_{i=1}^N T_{Li} g_i - T)$ , or equivalently  $T = \sum_{i=1}^N T_{Li} g_i - c \sum_{i=1}^N B_i g_i$ . Commonly, several crystalline phases coexist in a glass at equilibrium. Then we can write

$$c_j = \sum_{i=1}^N b_{ij} g_i (\sum_{i=1}^N T_{Lij} g_i - T) \quad (2)$$

where  $c_j$  is the  $j$ -th crystalline phase mass fraction,  $b_{ij}$  is the  $i$ -th component coefficient for the  $j$ -th crystalline phase, and  $T_{Lij}$  is the  $T_L$  coefficient for  $i$ -th component of  $j$ -th crystalline phase. Similarly,

$$T = \sum_{i=1}^N T_{Lij} g_i - c_j \sum_{i=1}^N B_{ij} g_i \quad (3)$$

where  $B_{ij}$  is the  $i$ -th component coefficient for the  $j$ -th crystalline phase. Note that the  $j$ -th crystalline phase "liquidus temperature",  $T_{Lj}$ , is given by the equation

$$T_{Lj} = \sum_{i=1}^N T_{Lij} g_i \quad (4)$$

where  $T_{Lij}$  is obtained from Equation 2 and 3 for each crystalline phases. Equation 2 and 3 were fitted to data for which the linear regression allowed obtaining the sets of the  $T_{Lij}$ ,  $b_{ij}$  and  $B_{ij}$  coefficients.

Table 2 summarizes the component coefficients ( $b_{ij}$ ,  $B_{ij}$ ,  $c_i$  and  $T_{Li}$ ) from applying models to data. Equation 1 was applied for primary crystalline phase to find the true  $T_L$ ; the correlation coefficient ( $R^2$ ) was 0.893. By applying Equation 2 to Ce-borosilicate ( $\text{Ce}_3\text{BSi}_2\text{O}_{10}$ ) crystalline phase produced  $R^2$  and root mean square error ( $s$ ) values of 0.869 and 0.98, respectively; while applying Equation 3 produced  $R^2$  and  $s$  values of 0.849 and 1.03, respectively. These equations were also applied to other crystalline phases separately. Corundum ( $\text{Al}_2\text{O}_3$ ) and mullite ( $\text{Al}_10\text{Si}_2\text{O}_{19}$ ) were combined as Al-containing crystals since only the combined data allowed the first-order models to be fitted rather than the corundum and mullite data treated individually. Fitting Equations 2 and 3 to Al-containing crystals resulted in  $R^2$  values of 0.852 and 0.846, respectively; while produced  $s$  values of 0.61 and 0.63, respectively.

With Ce-borosilicate primary phase, the measured  $T_L$  values ranged from 1094°C to 1280°C. For LABS-Sr glasses, the  $T_L$  values were between 1153 and 1405°C with either  $\text{RE}_3\text{BSi}_2\text{O}_{10}$ ,  $\text{Al}_2\text{O}_3$ , or  $\text{Al}_6\text{Si}_2\text{O}_{13}$  as the primary phases [1,2]. The Ce-borosilicate was the dominant crystalline phase in our LABS glasses. As the  $T_{L,i}$  coefficients shown in Table 2 as  $T_{L,i,r}$ ,  $T_{L,i,b}$ , and  $T_{L,i,B}$  (using three different methods of fitting) indicate, increasing fractions of  $\text{SiO}_2$  and  $\text{B}_2\text{O}_3$  in glass have a decreasing effect of  $T_L$  whereas  $\text{Al}_2\text{O}_3$ ,  $\text{CeO}_2$ , and  $\text{Nd}_2\text{O}_3$  promote crystallization (increase  $T_L$ ). In the LABS-Sr glasses [2], the  $T_L$  decreased as  $\text{SiO}_2$  and  $\text{B}_2\text{O}_3$ , and also  $\text{Al}_2\text{O}_3$ , increased, while the RE components had similar effects on  $T_L$  as in the LABS glasses under study.

In case of Al-containing crystal, the  $T_L$  values, which ranged from 1025 to 1398°C, were obtained by extrapolation based on Al-containing crystal fractions. A previous study [2] reported measured  $T_L$  of Al-silicate crystals within the range from 1164 to 1255°C and for  $\text{Al}_2\text{O}_3$  crystals from 1242 to 1305°C. On the other hand, Al-containing crystal model fitting showed better agreement with the data for Equation 2 than Equation 3, as well as for Ce-borosilicate model fitting, given by high  $R^2$  and low  $s$  values. As the coefficients indicate for Al-containing crystals, adding  $\text{SiO}_2$  and  $\text{B}_2\text{O}_3$  to glass has a tendency to decrease  $T_L$ , an increased  $\text{Al}_2\text{O}_3$  content has a moderate tendency to increase  $T_L$ , and  $\text{CeO}_2$  and  $\text{Nd}_2\text{O}_3$  have a strong tendency to increase  $T_L$ . In all glasses,  $\text{CeO}_2$  crystals appeared at a nearly constant fraction, indicating that they might form during cooling. The models described previously were applicable to several major phases, but the  $\text{CeO}_2$  crystalline phase was an exception. Its content was virtually independent of temperature, but was affected by glass composition. The following equation was used:

$$c_j = \sum_{i=1}^N c_{ij} g_i \quad (5)$$

where  $j \equiv \text{CeO}_2$ . Equation 5 was fitted to 136 data points ( $R^2 = 0.77$  and  $s = 0.33$ ). The coefficient values (shown in Table II) indicate that  $\text{CeO}_2$  crystallization decreased with increasing  $\text{SiO}_2$  and  $\text{B}_2\text{O}_3$  fractions and, as expected, increased with increasing  $\text{CeO}_2$  fraction, whereas  $\text{Al}_2\text{O}_3$  and  $\text{Nd}_2\text{O}_3$  fractions had a moderate effect.

## CONCLUSION

First-order models were fitted to the experimental dataset to obtain the fractions of individual crystalline phases as functions of temperature and glass composition (mass fractions of oxides), determining the  $T_L$  as the maximum temperature at which the crystal fraction was zero at equilibrium. Generally, the  $T_L$  increased as  $\text{SiO}_2$  and  $\text{B}_2\text{O}_3$  fraction decreased and  $\text{CeO}_2$ ,  $\text{Nd}_2\text{O}_3$ , and  $\text{Al}_2\text{O}_3$  increased. These components had a similar effect on the crystallization of  $\text{CeO}_2$ , which, however, was not affected by temperature and is suspected to precipitate during glass quenching. The models treat the coexisting major crystalline phases individually (except Al-containing phases, whose fractions were summed up), ignoring their interactions through their effects on matrix glass composition.

**Table II.** Component coefficients ( $b_{ij}$ ,  $B_{ij}$ ,  $c_i$  and  $T_{Li}$ ) for crystalline phases

Crystalline phase	Component	$b_{ij}$	$B_{ij}$	$c_i$	$T_{Li,r}$	$T_{Li,b}$	$T_{Li,B}$
Ce <sub>3</sub> BSi <sub>2</sub> O <sub>10</sub>	SiO <sub>2</sub>	0.008	-2005	-	344	167	317
	B <sub>2</sub> O <sub>3</sub>	0.010	-2875	-	-448	-1585	-1327
	Al <sub>2</sub> O <sub>3</sub>	-0.001	1537	-	1355	1516	1410
	CeO <sub>2</sub>	-0.002	3001	-	1701	1716	1738
	Nd <sub>2</sub> O <sub>3</sub>	-0.001	1400	-	1751	2055	1940
Al <sub>10</sub> Si <sub>2</sub> O <sub>19</sub> +Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	0.004	-3909	-	-	210	609
	B <sub>2</sub> O <sub>3</sub>	0.003	-2234	-	-	-1994	-1856
	Al <sub>2</sub> O <sub>3</sub>	0.001	-3919	-	-	2827	2492
	CeO <sub>2</sub>	-0.002	11456	-	-	1547	1664
	Nd <sub>2</sub> O <sub>3</sub>	0.000	3613	-	-	1582	1435
CeO <sub>2</sub>	SiO <sub>2</sub>	-	-	-0.084	-	-	-
	B <sub>2</sub> O <sub>3</sub>	-	-	-0.193	-	-	-
	Al <sub>2</sub> O <sub>3</sub>	-	-	0.013	-	-	-
	CeO <sub>2</sub>	-	-	0.183	-	-	-
	Nd <sub>2</sub> O <sub>3</sub>	-	-	0.030	-	-	-

(Subscript:  $r$  = fitting to first-order model (Equation 1),  $b$  = fitting to obtain  $b_i$  coefficients (Equation 2),  $B$  = fitting to obtain  $B_i$  coefficients (Equation 3))

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