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Liquidus temperature (TL) and crystal identification of glass containing rare-earth oxides

Prepared for the U.S. Department of Energy
Assistant Secretary for Environmental Management

Office of River Protection
P.O. Box 450
Richland, Washington 99352

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A. A. Kruger
Department of Energy - Office of River Protection

P. Hrma
POSTECH

S. M. Fadzil
POSTECH

J. Crum
Pacific Northwest National Laboratory

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Transactions of the Korean Nuclear Society Spring Meeting
Gwangju, Korea, May 30-31, 2013

Liquidus temperature (T_L) and crystal identification of glass containing rare-earth oxides

Syazwani Mohd Fadzil[a*], Pavel Hrma[a,b], Jarrod Crum[b]
[a] *Division of Advanced Nuclear Engineering, Pohang University of Science and Technology (POSTECH), Pohang, South Korea*
[b] *Pacific Northwest National Laboratory, Richland, Washington, United States*
[*]*Corresponding author: mfsyazwani86@postech.ac.kr*

1. Introduction

Pyrochemical process is a promising technique to reprocess the spent nuclear fuel that eliminates proliferation risk. Unlike the direct disposal of spent nuclear fuel, a low-cost and easier way, reprocessing increases utilization of resources and removes heat emitting elements from the waste [1, 2]. In this reprocessing method that includes four unit processes (voloxidation, electroreduction, electrorefining, and electrowinning) together with waste salt treatment process; final waste will be produced in form of a solid waste.

High level waste is usually stabilized in borosilicate glass by vitrification. The induction-heated furnace can operate at temperatures as high as 1400-1500°C. The melt is, poured into solidification drums and subjected to a heat-treatment to prevent cracking [3]. Precipitation of crystals from the melt can cause problems for melter operation and can compromise the product quality.

Currently, we study crystallization from a simplified borosilicate glass of composition (in mass%) 50.6 SiO_2 – 15.6 B_2O_3 – 10.9 Na_2O – 5.4 Al_2O_3 – 4.5 CaO – 2.9 ZrO_2. This simplified glass had also been used by Quintas et al. (2007) [4] with different composition and revealed crystallization of apatite during slow cooling; while Bardez et al. (2004) [5] characterize the glass structure on rare-earth surroundings. In this work, we prepared a glass with 10% La_2O_3 as a surrogate of the rare-earth mixture separated from molten salts used in pyroprocessing. We have determined the liquidus temperature (T_L) of this glass as well as equilibrium fractions of crystalline phases precipitated below T_L. Based on a previous study of glasses with the spinel primary crystallization phase [6], we used the equilibrium crystallinity to estimate the effect of oxides present in the crystals on the T_L.

2. Methods and Results

2.1 Fabrication of glass

The glass was prepared by batching from reagent chemical of SiO_2, Al_2O_3, H_3BO_3, ZrO_2, $CaCO_3$, Na_2CO_3 and La_2O_3, mixing in an agate mill, melting at 1300°C for 1 hour, cooling in air to room temperature, crushing in tungsten carbide mill, and remelting. To determine T_L, the glass was then heat-treated for 24 hours at different temperatures from 800°C to 1000°C. The samples were analyzed with optical microscope (OM), scanning electron microscope (SEM) with energy dispersive spectroscopy (EDS), and x-ray diffraction (XRD) [7].

2.2 Scanning electron microscope (SEM) with energy dispersive spectra (EDS)

Polished thin-sections of glass samples were coated with platinum and observed with SEM, Fig. 1. Table 1 shows the crystal composition obtained by EDS.

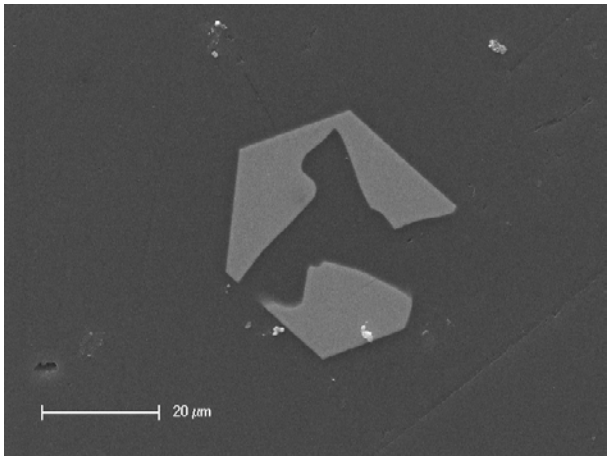

Fig. 1. Image of crystal in glass with 10% La_2O_3 heat-treated at 950°C.

Table 1. Composition of crystal and glass in mass%.

Region	Element (wt%)					
	O	Na	Al	Si	Ca	La
Crystal	16.18	1.05	0.78	14.35	0.46	55.01
Glass	29.68	8.61	4.99	35.95	3.81	7.47

2.3 X-ray diffraction (XRD)

Crushed samples were mixed with 5% CaF_2 as internal standard. Jade software identified in XRD patterns crystalline structure of oxyapatite ($CaLa_4Si_3O_{13}$) and Ce-stillwellite. Because the RE oxide in the glass was La_2O_3, we assume that the crystal was in fact the La-stillwellite, $LaBSiO_5$. Table 2 lists the crystal compositions obtained with TOPAS software.

Fig. 2 shows a graph of the total fraction of crystals in glass versus the heat-treatment temperature. The intercept of the trend line with the T-axis determines the

T_L as the maximum temperature at which glass and primary crystalline phase is in equilibrium [6]; T_L, = 958°C.

Table 2. Compositions of crystals in mass% as functions of heat-treatment temperature.

Temperature (°C)	Mass fraction		
	Oxyapatite	Stillwellite-(La)	Total crystal
950	0.021	0.172	0.193
900	0.121	1.508	1.629
850	1.540	1.315	2.855

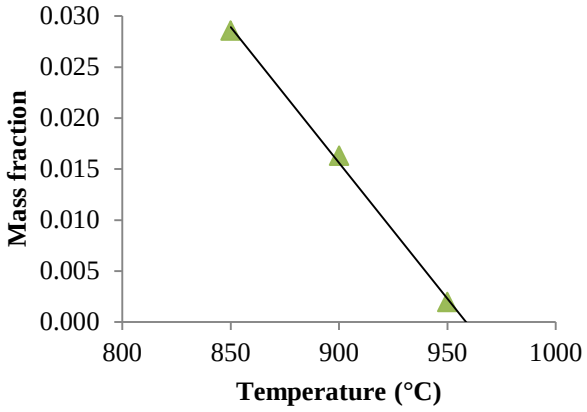

Fig. 2. Total crystalline phase mass fraction against heat-treatment temperature.

Apatite crystals, $Ca_2RE_8(SiO_4)_6O_2$, were identified in a slowly cooled borosilicate melt [4] and $RE_3BSi_2O_{10}$ crystals formed in glasses containing rare-earths as surrogated for Am and Cm [7]. In our study, $LaBSiO_5$ was the primary crystalline phase; the oxyapatite, $CaLa_4Si_3O_{13}$, began to form at temperatures below T_L.

Using a method described in Ref. [6], we computed the component coefficients for T_L, obtaining T_{B2O3} = 963°C, T_{SiO2} = 77°C. and T_{La2O3} = 7694°C. For the matrix glass that was in equilibrium with crystals, the T_L was the heat-treatment temperature. Estimating the T_L of these glasses using the component coefficient above, we reached a good agreement seen in Fig. 3.

3. Conclusions

This work had been carried out for only 10% addition of La in glass composition to find the T_L which is 958°C by assumption of one crystal phase. However, the calculated value of T_L, can be carried out with the result from XRD, EDS, equations and assumptions by previous study, agreed well with the measured T_L value. The phases identified by XRD are oxyapatite ($CaLa_4Si_3O_{13}$) and stillwellite ($LaBSiO_5$).

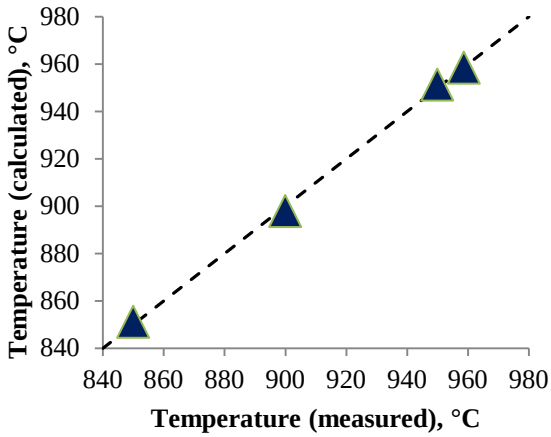

Fig. 3. Calculated T_L against measured T_L; and the identity line.

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