PREPARATION AND CHARACTERIZATION OF PU AND HF BEARING LANTHANIDE BOROILICATE AND ALUMINOBOROSILICATE GLASSES – 15667

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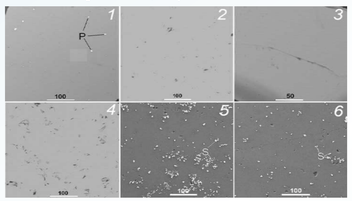
ABSTRACT

Eight borosilicate glasses with LaBS and ABS compositions containing plutonium and/or hafnium as a plutonium surrogate were prepared in Pt ampoules (Pu-bearing) and alumina or Pt crucibles (Hf-bearing) and characterized by X-ray diffraction, optical and scanning electron microscopy, infrared and Raman spectroscopy. Hf-bearing LaBS glasses were found to be amorphous whereas Pu-bearing glasses contained trace of plutonium dioxide and britholite. Hf and Fe bearing ABS glasses contained minor spinel structure phase. As followed from optical and SEM studies Hf-bearing LaBS glasses were more homogeneous than Pu-bearing and ABS glasses. The structure of the anionic motif of the glasses investigated by IR and Raman spectroscopy is typical of the glasses with relatively low silica content.

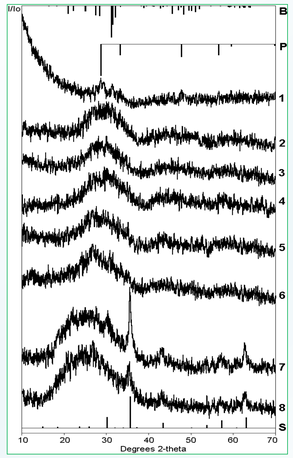
Target Chemical Compositions of the LaBS Glasses

Oxides	Frit X with PuO_2 (1)		Frit X with HfO_2 (2)		Frit X with PuO_2 (3)		Frit X with HfO_2 (4)		Frit A with HfO_2 (5)		Frit A with HfO_2 (6)		Frit ABS with HfO_2 (7)		Frit ABS with HfO_2 (8)	
	mol.%	wt.%	mol.%	wt.%	mol.%	wt.%	mol.%	wt.%	mol.%	wt.%	mol.%	wt.%	mol.%	wt.%	mol.%	wt.%
Li_2O	-	-	-	-	-	-	-	-	-	-	-	-	10.8	4.9	10.9	5.0
B_2O_3	21.8	11.8	21.8	12.0	22.4	12.4	22.4	12.5	16.2	10.8	16.5	11.2	5.6	5.9	5.6	6.0
Na_2O	-	-	-	-	-	-	-	-	-	-	-	-	14.6	13.8	14.7	14.0
Al_2O_3	11.4	9.0	11.4	9.2	11.8	9.5	11.8	9.6	20.3	19.8	20.7	20.7	5.7	8.8	5.7	8.9
SiO_2	39.1	18.1	39.1	18.6	39.9	19.0	39.9	19.2	46.8	27.0	47.7	28.0	53.7	49.1	53.9	49.7
CaO	-	-	-	-	-	-	-	-	-	-	-	-	2.4	2.0	2.3	2.0
MnO	-	-	-	-	-	-	-	-	-	-	-	-	1.9	2.0	1.8	2.0
Fe_2O_3	-	-	-	-	-	-	-	-	-	-	-	-	4.9	11.9	4.9	12.0
SrO	2.9	2.3	2.9	2.4	2.9	2.4	2.9	2.4	2.4	2.4	2.4	2.4	-	-	-	-
ZrO_2	-	-	-	-	-	-	-	-	1.0	1.2	1	1.2	-	-	-	-
La_2O_3	6.8	17.2	6.8	17.5	7.0	18.1	7.0	18.3	3.7	11.4	3.8	11.9	-	-	-	-
Nd_2O_3	5.2	13.6	5.2	13.8	5.3	14.3	5.3	14.4	3.7	11.9	3.7	12.4	-	-	-	-
Gd_2O_3	4.4	12.2	4.4	12.6	4.5	12.8	4.5	13.0	2.3	8.0	2.3	8.3	-	-	-	-
HfO_2	3.9	6.3	8.4	14.0	4.0	6.7	6.3	10.7	3.7	7.5	1.9	3.8	0.5	1.6	0.1	0.4
PuO_2	4.5	9.5	-	-	2.3	5.0	-	-	-	-	-	-	-	-	-	-
Sums	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

The glasses produced were examined with X-ray diffraction (XRD) using a Rigaku D/MAX-2200 diffractometer (Cu Kα radiation), optical microscopy using an OLYMPUS BX51 polarizing microscope (polished sections were prepared by smoothing on rotating mechanical disc using abrasives with grain size from 0.105 to 0.003 mm followed by polishing with a felt), scanning electron microscopy (SEM) using a Tescan Vega II XMU unit with an INCAx-sight energy dispersive X-ray (EDX) spectrometer, IR spectroscopy using a modernized IKS-29 spectrophotometer (compaction of powdered glass in pellets with KBr), and Raman spectroscopy using a Jobin Yvon U1000 spectrophotometer (excitation wavelength is 514,4 Å).

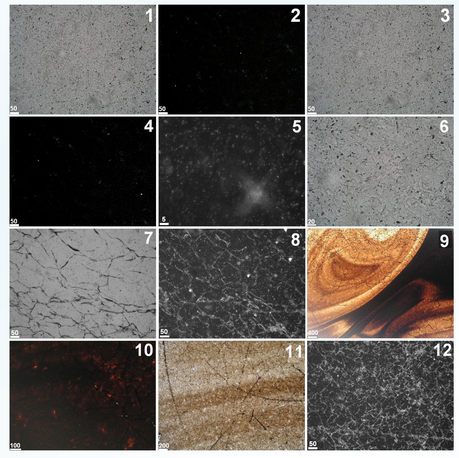


SEM Images in Backscattered Electrons of the Glasses ## 1 (1), 2 (2), 5(3), 6 (4), 7 (5), and 8 (6) Produced in Platinum Crucibles.
Glass ID is given in Table I. Scale bars are given in microns. P – pyrochlore/britholite, S – spinel.



XRD patterns of the glasses.

1-8 – Glass ID in Table I, B – britholite, P – PuO_2, S – spinel

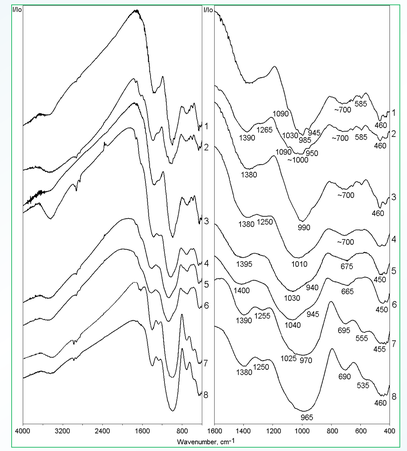


Optical Microscopic Images of the Glasses ##2 (1,2), 4 (3,4,5), 6 (6), 7 (7,8,9,10), and 8 (11,12) in Parallel (1,3,6,7,9,11) and Crossed Nichols (2,4,5,8,10,12).
Glass ID is given in Table. Scale bars are given in microns

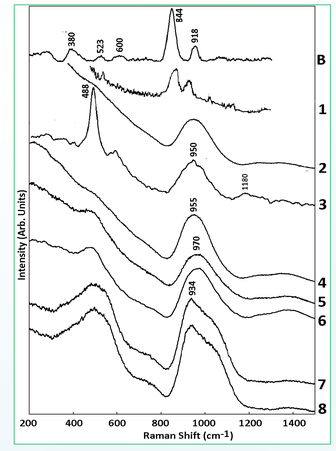
Chemical Compositions (wt.%) of Glasses #2, #6, #7 and #8 Produced in Alumina (Al) and Platinum (Pt) Crucibles Determined by EDX

Oxides	2			6			7			8		
	Target	Al	Pt	Target	Al	Pt	Target	Al	Pt	Target	Al	Pt
Li_2O*	-	-	-	-	-	-	4.9	4.6	4.9	5.0	4,7	5.0
B_2O_3*	12.0	4.8	11.7	11.2	7.3	10.9	5.9	5.6	5.9	6.0	5,6	6.0
Na_2O	-	-	-	-	-	-	13.8	10.0	13.8	14.0	10,5	13.9
Al_2O_3	9.2	23.7	9.3	20.7	22.5	20.9	8.8	27.8	8.9	8.9	26,9	9.0
SiO_2	18.6	18.7	18.7	28.0	33.5	28.1	49.1	39.1	49.2	49.7	40,7	49.7
CaO	-	-	-	-	-	-	2.0	1.6	2.0	2.0	1,7	2.0
MnO	-	-	-	-	-	-	2.0	1.6	2.1	2.0	1,4	2.0
Fe_2O_3 /FeO	-	-	-	-	-	-	11.9	8.3	12.0	12.0	8,0	12.1
SrO	2.4	1.7	2.4	2.4	2.9	2.4	-	-	-	-		-
ZrO_2	-	-	-	1.2	1.4	1.3	-	-	-	-		-
La_2O_3	17.5	15.5	17.6	11.9	11.1	12.0	-	-	-	-		-
Nd_2O_3	13.8	11.6	13.8	12.4	10.6	12.4	-	-	-	-		-
Gd_2O_3	12.6	11.4	12.6	8.3	7.2	8.3	-	-	-	-		-
HfO_2	14.0	12.6	13.9	3.8	3.5	3.9	1.6	1.3	1.6	0.4	0,6	0.5
Sums	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.4	100.0	100,0	100.2

* Li and B are not determined by EDX; for glasses #2 and #6 B_2O_3 concentrations were calculated by difference 100% - Sum of other oxides; for glasses #7 and #8 the target values are given.



IR Spectra of the LaBS Glasses Produced in Pt Crucibles.
1-8 – Glass ID in Table I.



Raman Spectra of LaBS Glasses Produced in Pt Crucibles.
1-8 – Glass ID in Table I, B – britholite

CONCLUSION

Glasses for Pu immobilization were prepared using three Frit compositions: REE_2O_3- bearing aluminoborosilicate Frit X, high-Al_2O_3 REE_2O_3-bearing aluminoborosilicate Frit A, and lithium-sodium borosilicate Frit ABS. The as-prepared Frit X based glass with 9.5 wt.% PuO_2 (#1) contained trace of PuO_2 and britholite, the Frit X and Frit A based glasses ## 2-6 were fully amorphous, although glass #3 (5.0 wt.% PuO_2) may contain trace of PuO_2 and britholite as well. Glasses ##7 and 8 (Fe-bearing) produced using Li-Na-B-Si Frit ABS contained minor spinel structure phase or crystallites formed at the early stage of crystallization. HfO_2 seems to be some more soluble in borosilicate glasses than PuO_2 and Hf-bearing glasses were found to be more homogeneous than the Pu-bearing at the same molar oxide concentrations of HfO_2 and PuO_2. Incorporation of Fe_2O_3 in the LaBS glasses results in textural non-uniformity of the glasses and formation of microcrystals of magnetite-type spinel. As follows from IR and Raman spectra the glasses based on Frit X are the most structured and have a tendency to chemical differentiation with formation of chemically and structurally ordered microareas as it is seen from the splitting of absorption bands in IR spectra. Raman spectrum of the glass with the highest PuO_2 content demonstrates appreciable contribution of the spectrum due to britholite. The glasses based on Frit A are much more homogeneous; glasses based on Frit ABS have compositionally uniform matrix with minor fine spinel crystals distributed within its bulk and their anionic motif is closer on structure to borosilicate glasses containing high-Fe SRS SB2 and SB4 surrogates

ACKNOWLEDGEMENT

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