XRD, ELECTRON MICROSCOPY AND VIBRATIONAL SPECTROSCOPY

CHARACTERIZATION OF SIMULATED HIGH-FE/AL HLW GLASSES – 15666

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ABSTRACT

Sample glasses have been made using SB6 high level waste (HLW) simulant (high in both Al and Fe) with 12 different frit compositions at a constant waste loading of 36 wt.%. As follows from X-ray diffraction (XRD) and optical and scanning electron microscopy (SEM) data, all the samples are composed of primarily glass and minor concentration of spinel phases which form both isometric grains and fine cubic (~1 μm) crystals. Infrared (IR) spectra of all the glasses within the range of 400-1600 cm^{-1} consist of the bands due to stretching and bending modes in silicon-oxygen, boron-oxygen, aluminum-oxygen and iron-oxygen structural groups. Raman spectra showed that for the spectra of all the glasses within the range of 850-1200 cm^{-1} the best fit is achieved by suggestion of overlapping of three major components with maxima at 911-936 cm^{-1}, 988-996 cm^{-1} and 1020-1045 cm^{-1}. The structural network is primarily composed of metasilicate chains and possibly rings with embedded AlO_4 and FeO_4 tetrahedra. Major BO_4 tetrahedra and BO_3 triangles form complex borate units and are present as separate constituents.

The objective of this work is to apply the insight gained from studying the impact of varying levels of boron, alkali, and some additives such as Ca and Mn on the coordination chemistry of simulated HLW glass systems using different methods such as IR and Raman spectroscopy.

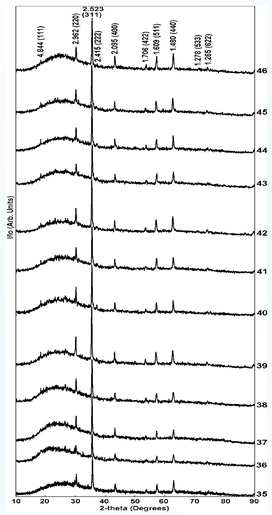
Chemical Composition of SB6-CEF Surrogate

Elements	wt.%	Oxides	wt.%
Fe	18.90	Fe_2O_3	27.02
Al	15.90	Al_2O_3	29.05
Mn	5.92	MnO	7.64
Ca	0.95	CaO	1.33
Mg	0.45	MgO	0.75
Ni	2.54	NiO	3.23
Cu	0.18	CuO	0.23
Ti	0.01	TiO_2	0.02
Si	0.14	SiO_2	0.30
Na	15.40	Na_2O	20.76
K	0.07	K_2O	0.08
Sr	0.05	SrO	0.06
Zr	0.21	ZrO_2	0.29
S	0.37	SO_3	0.92
Total	61.09	Total	91.68

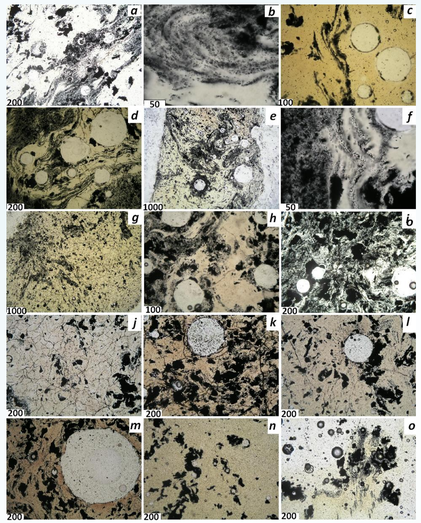
Glass compositions

Oxides	35		36		37		38		39		40		41		42		43		44		45		46	
	wt. %	mol. %	wt. %	mol. %	wt. %	mol. %	wt. %	mol. %	wt. %	mol. %	wt. %	mol. %	wt. %	mol. %	wt. %	mol. %	wt. %	mol. %	wt. %	mol. %	wt. %	mol. %	wt. %	mol. %
Li_2O	5.12	11.41	5.12	11.47	5.12	11.44	5.12	11.46	5.76	12.83	5.12	11.42	5.12	11.43	5.12	11.45	5.12	11.41	5.12	11.42	5.12	11.44	5.12	11.49
B_2O_3	5.12	4.90	8.96	8.62	7.04	6.75	7.04	6.76	7.04	6.73	5.12	4.90	5.12	4.91	5.12	4.91	5.12	4.89	5.12	4.90	5.12	4.91	10.24	9.86
Na_2O	12.59	13.52	12.59	13.60	12.59	13.56	11.31	12.20	10.67	11.45	12.59	13.54	11.95	12.86	11.31	12.20	11.95	12.83	11.31	12.16	11.31	12.18	10.03	10.85
MgO	0.27	0.45	0.27	0.45	0.27	0.45	0.27	0.45	0.27	0.45	0.27	0.45	0.27	0.45	0.27	0.45	0.27	0.45	0.27	0.45	0.27	0.45	0.27	0.45
Al_2O_3	10.78	7.04	10.78	7.08	10.78	7.06	10.78	7.07	10.78	7.03	10.78	7.05	10.78	7.05	10.78	7.07	10.78	7.04	10.78	7.04	10.78	7.06	10.78	7.09
SiO_2	48.75	54.01	44.91	50.05	46.83	52.03	46.83	52.12	45.55	50.43	48.11	53.36	48.11	53.40	47.47	52.80	47.47	52.58	47.47	52.63	46.19	51.32	46.19	51.53
SO_3	0.33	0.27	0.33	0.28	0.33	0.28	0.33	0.28	0.33	0.27	0.33	0.27	0.33	0.27	0.33	0.28	0.33	0.27	0.33	0.27	0.33	0.28	0.33	0.28
K_2O	0.03	0.02	0.03	0.02	0.03	0.02	0.03	0.02	0.03	0.02	0.03	0.02	0.03	0.02	0.03	0.02	0.03	0.02	0.03	0.02	0.03	0.02	0.03	0.02
CaO	0.48	0.57	0.48	0.57	0.48	0.57	0.48	0.57	0.48	0.57	0.48	0.57	0.48	0.57	0.48	0.57	1.76	2.09	1.76	2.09	1.76	2.10	0.48	0.57
TiO_2	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
MnO	2.75	2.58	2.75	2.60	2.75	2.59	4.03	3.80	5.31	4.98	3.39	3.18	4.03	3.79	5.31	5.00	3.39	3.18	4.03	3.78	5.31	5.00	2.75	2.60
Fe_2O_3	9.73	4.06	9.73	4.08	9.73	4.07	9.73	4.07	9.73	4.05	9.73	4.06	9.73	4.06	9.73	4.07	9.73	4.06	9.73	4.06	9.73	4.07	9.73	4.08
NiO	1.16	1.03	1.16	1.04	1.16	1.04	1.16	1.04	1.16	1.03	1.16	1.04	1.16	1.04	1.16	1.04	1.16	1.03	1.16	1.03	1.16	1.04	1.16	1.04
CuO	0.08	0.07	0.08	0.07	0.08	0.07	0.08	0.07	0.08	0.07	0.08	0.07	0.08	0.07	0.08	0.07	0.08	0.07	0.08	0.07	0.08	0.07	0.08	0.07
SrO	0.02	0.01	0.02	0.01	0.02	0.01	0.02	0.01	0.02	0.01	0.02	0.01	0.02	0.01	0.02	0.01	0.02	0.01	0.02	0.01	0.02	0.01	0.02	0.01
ZrO_2	0.11	0.06	0.11	0.06	0.11	0.06	0.11	0.06	0.11	0.06	0.11	0.06	0.11	0.06	0.11	0.06	0.11	0.06	0.11	0.06	0.11	0.06	0.11	0.06
Sum	97.33	100.0	97.33	100.0	97.33	100.0	97.33	100.0	97.33	100.0	97.33	100.0	97.22	100.0	97.33	100.0	97.33	100.0	97.33	100.0	97.33	100.0	97.33	100.0
ψ_B		2,14		1.22		1.56		1.35		1.25		2.14		2.00		1.86		2.00		1.86		1.86		0.79
ψ_B(Fe)*		1.89		1.08		1.37		1.17		1.07		1.89		1.75		1.61		1.75		1.61		1.61		0.66
K		11.0		5.8		7.7		7.7		7.5		10.9		10.9		10.8		10.8		10.7		10.5		5.2

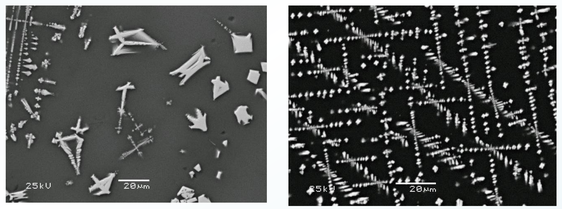
* $\psi_B(Fe) = \{(Na_2O+K_2O+BaO)+[0.7(CaO+SrO+CdO+PbO)+[0.3(Li_2O+ MgO+ZnO)]-Al_2O_3-0.3Fe_2O_3\} / B_2O_3$



XRD patterns of the samples. All the reflections are due to spinel



Optical microscopy images of the samples. Scale bars are given in microns



(a) *(b)*

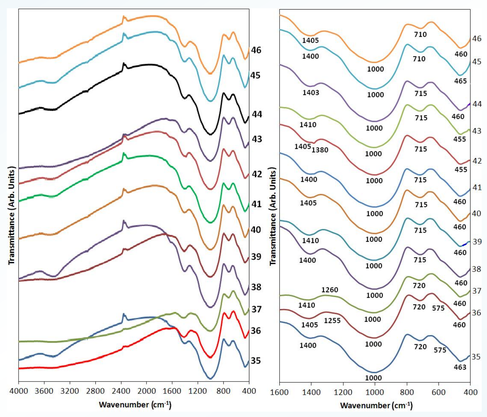
Primary (a) and secondary (b) spinels in glass

The major features of all the samples are as follows:

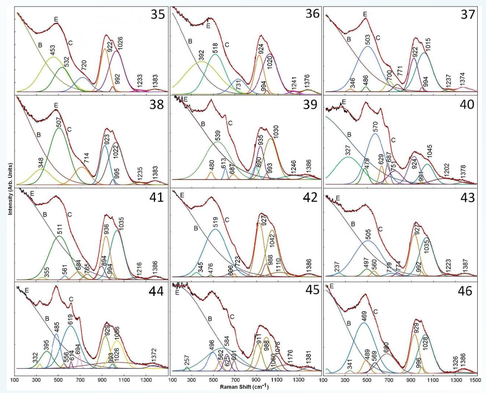
- All the samples are composed of primarily glassy phase and minor spinel phases;
- All the samples contain gas bubbles with variable diameter (from <10 μm to >1 mm) due to incomplete refining;
- Coloring of glass varies from nearly clear to brown;
- Spinel forms both isometric grains and fine cubic crystals (~1 μm);
- Microcrystals are aggregated in bands with variable glass and spinel contents;
- Relative location of the bands is caused by flowing of various portions of the glass melt with varying viscosity;
- Wavy profile of the bands is similar to that in volcanic glasses with fluidal texture;
- No devitrification of the glass (crystallization of silicates) was found.

Major differences between the samples are as follows:

- The samples (possibly various regions of the same sample) are different in quantitative glass to spinel ratio;
- Significant differences was found in the ratio of isometric grains to cubic microcrystals;
- Fluidal texture varies; in some samples fluidity takes place only in local areas or is entirely absent;
- Degree of cracking in the thin sections varies widely. Major cracks were probably formed at preparation of the thin sections for microscopic studies.



IR spectra of the glass samples (left) and their fragments (right)



Raman spectra of the samples and their deconvolution. B – baseline, C – smoothed line, E – experimental spectrum

CONCLUSION

All the glasses studied are composed of predominantly vitreous phase and minor spinel structure phase. Spinel forms both isometric grains and cubic microcrystals (~1 μm). Microcrystals are aggregated in bands with variable glass and spinel contents. IR and Raman spectroscopic study revealed that the structure of all the glasses are similar and are composed of metasilicate chains and rings containing incorporated AlO_4 and FeO_4 as well as minor BO_4 tetrahedra. FeO_6 octahedral units may also be present. In the structure of all the glasses, trigonally-coordinated boron dominates over tetrahedrally-coordinated boron. With that said, major BO_4 tetrahedra and BO_3 triangles form complex borate units and are present as separate constituents.

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