

Table I: Composition of halogen-free and halogen-bearing glasses determined by electron microprobe. The analysis of each glass is based on the average of 10 measurements with the standard deviation (σ). Standards were: albite (Na), sanidine (K), wollastonite (Ca, Si), titanium dioxide (Ti), rhodonite (Mn), hematite (Fe), sodium chloride (Cl), olivine (Mg), anorthite (Al) and topaz (F).

Oxides/ ions mol%	BA-0	BA-Cl	BA-Cl-2	BA-Cl-3	BA-Cl-4	BA-Cl-F	BA-Cl-F-2	BA-Cl-F-3	BA-F	BA-F-2
SiO ₂	54.97 ±0.16	54.01 ±0.15	54.34 ±0.16	53.89 ±0.15	54.18 ±0.15	53.40 ±0.14	51.41 ±0.12	51.95 ±0.15	53.72 ±0.16	50.73 ±0.12
Na ₂ O	4.68 ±0.08	3.85 ±0.08	3.59 ±0.05	4.08 ±0.06	4.26 ±0.05	3.78 ±0.05	3.62 ±0.02	4.02 ±0.04	4.50 ±0.05	4.25 ±0.04
K ₂ O	0.16 ±0.02	0.13 ±0.02	0.09 ±0.03	0.13 ±0.02	0.15 ±0.01	0.12 ±0.03	0.11 ±0.04	0.14 ±0.02	0.17 ±0.03	0.15 ±0.03
TiO ₂	1.07 ±0.03	1.04 ±0.05	1.04 ±0.05	1.02 ±0.04	1.04 ±0.04	1.04 ±0.04	1.00 ±0.03	0.99 ±0.05	1.06 ±0.05	0.98 ±0.04
FeO _{total}	2.54 ±0.12	2.39 ±0.07	2.25 ±0.13	2.73 ±0.05	1.92 ±0.12	2.41 ±0.08	2.27 ±0.10	2.79 ±0.07	2.44 ±0.13	2.25 ±0.07
Al ₂ O ₃	9.52 ±0.09	9.31 ±0.05	9.39 ±0.05	9.14 ±0.06	9.22 ±0.06	9.23 ±0.05	8.95 ±0.06	8.84 ±0.06	9.35 ±0.05	8.81 ±0.04
MgO	12.75 ±0.07	12.39 ±0.07	12.38 ±0.06	12.35 ±0.08	12.43 ±0.09	12.29 ±0.08	11.81 ±0.08	11.94 ±0.10	12.54 ±0.09	11.67 ±0.07
CaO	14.13 ±0.09	13.81 ±0.10	14.12 ±0.09	13.87 ±0.08	14.04 ±0.03	14.28 ±0.10	13.47 ±0.05	13.53 ±0.05	13.82 ±0.04	13.26 ±0.10
MnO	0.16 ±0.03	0.15 ±0.04	0.14 ±0.02	0.15 ±0.02	0.16 ±0.02	0.16 ±0.03	0.15 ±0.02	0.17 ±0.02	0.18 ±0.02	0.16 ±0.01
Cl ⁻	0.02 ±0.01	2.82 ±0.01	2.53 ±0.01	2.73 ±0.02	1.92 ±0.02	2.15 ±0.02	1.96 ±0.01	3.28 ±0.01	0.00 ±0.01	0.02 ±0.03
F ⁻	0.00 ±0.00	0.12 ±0.01	0.13 ±0.00	0.00 ±0.04	0.00 ±0.04	1.13 ±0.04	5.25 ±0.10	2.35 ±0.02	2.24 ±0.02	7.73 ±0.08
γ ^[1]	0.78	0.77	0.77	0.78	0.78	0.78	0.7	0.78	0.78	0.78
NBO/T ^[2]	0.45	0.42	0.41	0.43	0.44	0.43	0.42	0.45	0.44	0.43
NBO/T ^[3]	0.45	0.47	0.45	0.48	0.47	0.48	0.54	0.55	0.47	0.46

^[1] γ is an indicator for the degree of polymerisation of the melt (Webb et al. 2014)

$$\gamma = (\text{Na}_2\text{O} + \text{K}_2\text{O} + \text{MnO} + \text{FeO} + \text{CaO} + \text{MgO}) / (\text{Na}_2\text{O} + \text{K}_2\text{O} + \text{MnO} + \text{FeO} + \text{CaO} + \text{MgO} + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3)$$

^[2] NBO/T calculated without halogens (chlorine and fluorine)

^[3] NBO/T calculated assuming $2\text{Cl}^- = 1\text{O}^{2-}$ or $2\text{F}^- = 1\text{O}^{2-}$

Table II: Analysis of redox equilibrated halogen-free and -bearing glasses (electron microprobe). The measurement of each glass is based on average of 10 measurements with the standard deviation (σ). Standards were: albite (Na), sanidine (K), wollastonite (Ca, Si), titanium dioxide (Ti), rhodonite (Mn), hematite (Fe), sodium chloride (Cl), olivine (Mg), anorthite (Al) and topaz (F).

Oxides/ ions mol%	BA-0_N3	BA-0_N1	BA-0_N-1	BA-Cl_N3	BA-Cl_N1	BA-Cl_N-1	BA-Cl-F_N3	BA-Cl-F_N1	BA-Cl-F_N-1	BA-F_N3	BA-F_N1	BA-F_N-1
ΔNNO	+3	+1	-1	+3	+1	-1	+3	+1	-1	+3	+1	-1
$\log_{10}(f\text{O}_2)$ gas mixing	-4.97	-6.97	-8.97	-4.39	-6.39	-8.39	-4.39	-6.39	-8.39	-4.97	-6.97	-8.97
SiO ₂	54.42 ±0.30	54.57 ±0.24	54.39 ±0.30	55.53 ±0.30	54.88 ±0.20	54.70 ±0.28	54.45 ±0.32	54.09 ±0.30	54.12 ±0.22	53.36 ±0.30	53.05 ±0.26	53.21 ±0.26
Na ₂ O	4.40 ±0.10	4.48 ±0.12	4.50 ±0.06	3.73 ±0.08	3.61 ±0.04	3.51 ±0.02	3.51 ±0.10	4.04 ±0.12	3.72 ±0.12	4.57 ±0.10	4.55 ±0.18	4.37 ±0.08
K ₂ O	0.15 ±0.04	0.16 ±0.02	0.16 ±0.02	0.11 ±0.02	0.10 ±0.05	0.10 ±0.01	0.11 ±0.04	0.12 ±0.02	0.11 ±0.01	0.16 ±0.04	0.17 ±0.02	0.16 ±0.02
TiO ₂	1.05 ±0.06	1.07 ±0.06	1.03 ±0.10	1.06 ±0.06	1.07 ±0.02	1.06 ±0.02	1.05 ±0.06	1.04 ±0.06	1.04 ±0.02	1.05 ±0.04	1.04 ±0.04	1.02 ±0.08
FeO _{total}	3.18 ±0.09	2.89 ±0.12	3.14 ±0.13	3.35 ±0.20	2.80 ±0.15	2.71 ±0.08	3.06 ±0.14	3.66 ±0.12	3.49 ±0.16	3.48 ±0.08	3.85 ±0.20	3.26 ±0.16
Al ₂ O ₃	9.63 ±0.18	9.42 ±0.16	9.46 ±0.04	9.16 ±0.18	9.45 ±0.10	9.39 ±0.10	9.34 ±0.02	9.41 ±0.05	9.35 ±0.03	9.28 ±0.05	9.29 ±0.08	4.60 ±0.10
MgO	12.81 ±0.14	12.90 ±0.12	12.65 ±0.10	12.40 ±0.04	12.78 ±0.06	12.73 ±0.04	12.62 ±0.12	12.12 ±0.12	12.47 ±0.17	12.75 ±0.18	12.70 ±0.22	12.49 ±0.18
CaO	14.15 ±0.18	14.32 ±0.06	14.47 ±0.16	13.56 ±0.19	14.39 ±0.12	14.37 ±0.18	14.35 ±0.16	13.52 ±0.34	13.77 ±0.12	13.81 ±0.14	13.93 ±0.14	14.14 ±0.26
MnO	0.18 ±0.04	0.18 ±0.02	0.18 ±0.02	0.17 ±0.02	0.16 ±0.02	0.15 ±0.06	0.17 ±0.06	0.16 ±0.02	0.16 ±0.01	0.18 ±0.04	0.17 ±0.02	0.17 ±0.05
Cl ⁻	0.01 ±0.01	0.01 ±0.01	0.01 ±0.02	0.92 ±0.03	0.74 ±0.06	1.29 ±0.02	1.13 ±0.06	1.32 ±0.05	1.28 ±0.16	0.02 ±0.02	0.02 ±0.00	0.01 ±0.01
F ⁻	0.00 ±0.00	0.00 ±0.01	0.00 ±0.00	0.00 ±0.00	0.00 ±0.01	0.00 ±0.01	0.20 ±0.03	0.51 ±0.22	0.48 ±0.04	1.35 ±0.08	1.25 ±0.12	1.87 ±0.36
γ ^[1]	0.77	0.78	0.77	0.77	0.77	0.77	0.77	0.77	0.76	0.78	0.78	0.77
NBO/T ^[2]	0.49	0.52	0.54	0.45	0.48	0.49	0.45	0.48	0.51	0.49	0.53	0.53
NBO/T ^[3]	0.49	0.52	0.54	0.47	0.50	0.51	0.48	0.51	0.54	0.51	0.56	0.56

^[1] γ is an indicator for the degree of polymerisation of the melt (Webb et al. 2014)

$$\gamma = (\text{Na}_2\text{O} + \text{K}_2\text{O} + \text{MnO} + \text{FeO} + \text{CaO} + \text{MgO}) / (\text{Na}_2\text{O} + \text{K}_2\text{O} + \text{MnO} + \text{FeO} + \text{CaO} + \text{MgO} + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3)$$

^[2] NBO/T calculated without halogens (chlorine and fluorine)

^[3] NBO/T calculated assuming $2\text{Cl}^- = 1\text{O}^{2-}$ or $2\text{F}^- = 1\text{O}^{2-}$

Table III: Chemical composition of the starting glasses of series III analysed by electron microprobe. The analysis of each glass is based on the average of 10 measurements.

Oxides/ions mol%	BA-0-III	BA-Cl-III	BA-Cl-F-III	BA-F-III
SiO ₂	55.25 ±0.15	53.72 ±0.15	52.02 ±0.14	52.49 ±0.16
Na ₂ O	4.53 ±0.05	3.59 ±0.04	3.79 ±0.04	4.36 ±0.05
K ₂ O	0.17 ±0.02	0.10 ±0.01	0.12 ±0.02	0.16 ±0.02
TiO ₂	1.06 ± 0.03	1.04 ±0.03	1.00 ±0.02	0.99 ±0.03
FeO	2.44 ±0.06	2.33 ±0.06	2.49 ±0.08	2.29 ±0.06
Al ₂ O ₃	9.45 ±0.09	9.20 ±0.08	8.89 ±0.10	8.99 ±0.09
MgO	12.71 ±0.07	12.22 ±0.07	11.96 ±0.05	12.13 ±0.06
CaO	14.21 ±0.09	13.99 ±0.08	13.50 ±0.09	13.51 ±0.09
MnO	0.17 ±0.02	0.15 ±0.03	0.16 ±0.03	0.16 ±0.02
Cl ⁻	0.01 ±0.01	3.65 ±0.04	3.90 ±0.02	0.01 ±0.01
F ⁻	0.00 ±0.01	0.00 ±0.01	2.18 ±0.03	4.90 ±0.04
γ ^[1]	0.78	0.77	0.78	0.78
NBO/T ^[2]	0.315	0.314	0.326	0.315
NBO/T ^[3]	0.316	0.370	0.422	0.392

^[1] γ is an indicator for the degree of polymerisation of the melt (Webb et al. 2014)

$$\gamma = (\text{Na}_2\text{O} + \text{K}_2\text{O} + \text{MnO} + \text{FeO} + \text{CaO} + \text{MgO}) / (\text{Na}_2\text{O} + \text{K}_2\text{O} + \text{MnO} + \text{FeO} + \text{CaO} + \text{MgO} + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3)$$

^[2] NBO/T calculated without halogens (chlorine and fluorine)

^[3] NBO/T calculated assuming NBO/T calculated assuming $2\text{Cl}^- = 1\text{O}^{2-}$ or $2\text{F}^- = 1\text{O}^{2-}$

Table IV: H_2O_{total} content of thermogravimetry measurements and $CO_2_{(total)}$ content of CS measurements. The dry and CO_2 -bearing samples synthesised in IHPV have a water content ~ 0.10 wt% H_2O .

Sample	H_2O_{TGA} (wt%)	ΔH_2O_{TGA} (wt%)	Sample	CO_2_{CS} (ppm)	ΔCO_2_{CS} (ppm)
BA-0_0.73H	0.73	0.02	BA-0_0.15C	1479	14
BA-0_1.29H	1.27	0.05	BA-0_0.23C	2199	185
BA-0_3.47H	3.46	0.03			
BA-Cl_0.53H	0.53	0.05	BA-Cl_0.12C	1442	164
BA-Cl_1.76H	1.81	0.02	BA-Cl_0.37C	3658	35
BA-Cl_3.56H	3.44	0.02			
BA-Cl-F_0.59H	0.69	0.03	BA-Cl-F_0.14C	1234	211
BA-Cl-F_1.31H	1.53	0.02	BA-Cl-F_0.29C	2975	180
BA-Cl-F_3.50H	4.25	0.04			
BA-F_0.63H	0.58	0.02	BA-F_0.09C	1018	21
BA-F_1.84H	1.67	0.03	BA-F_0.20C	1853	34
BA-F_4.04H	3.57	0.02			