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Glass Characterization

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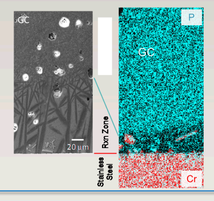
Sealing materials suffer from processing and performance complexities

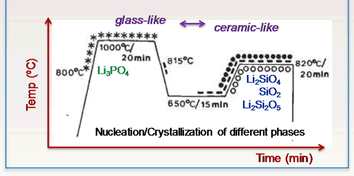
Glass for Glass-to-Metal (GtM) Sealing
+ Processability
+ Materials Compatibility
+ Durability
- Low CTE
- Low toughness/crack tolerance
- Reactivity & Stability

Alternatives to Glass for GtM Sealing
1) Glass-Ceramics + high CTE
+ ceramic-like properties
- complicated thermal processing to achieve microstructure
2) Filled-Glass Composites (FGCs) combine the attributes of a glass and a ceramic.
+ Glass processability
+ High/Tailorable CTE
+ Microstructural stability

Seal/Interface Is Adversely Affected By Interdiffusion & Devitrification



Glass-Ceramics - thermal processing determines microstructure)



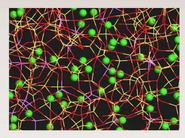
Hoodley & Hochman, "Crystallization of a Glass-Ceramic by Optical Growth", J Am Ceram Soc, 67 [9] 630-35 (1984).

Strategy is to develop FGCs with improved processability and properties

Our approach is to develop experimentally informed modeling/simulation tools to identify glass chemistry-structure-property relationships.

Stage 1

Characterize & model glass chemistry and structure
- 1st - In simple 3-component glass formulations
- 2nd - In more complex glasses
- 3rd – With fillers and at interfaces



Long-range disorder

Stage 2

Compare/contrast modeling & experimental results.
- Assess modeling sensitivities and experimental limitations.
- Inform and refine modeling and/or experiments.

Stage 3

Relate chemistry and structure to properties (density, CTE, T_g, …).

Stage 4

Design/Fabricate & characterize filled-glass composite sealing materials

Many sealing glass compositions are based on borosilicate or aluminosilicate compositions

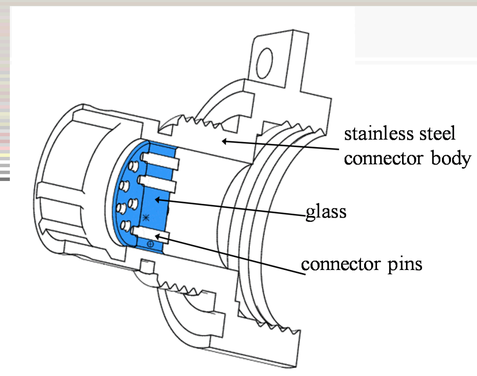
	#1 [at.%]	#2 [at.%]	#3 [at.%]	#4 [at.%]	#5 [at.%]	#6 [at.%]	#7 [at.%]	#8 [at.%]	#9 [at.%]	#10 [at.%]	#11 [at.%]	#12 [at.%]	#13 [at.%]	#14 [at.%]
Silicon	72	72	72	72	74	60	72	72	70	72	73	72	73	73
Barium	9	9	9	9	8	7	9	9	9	9	9	9	9	8
Na + K	15	15	14	14	12	11	15	15	17	15	13	14	13	15
Aluminum	4	4	5	4	5	22	4	4	4	4	4	4	4	4
Cobalt	0.23	0.23	0.22		0.21		0.24	0.27	0.31	0.23				

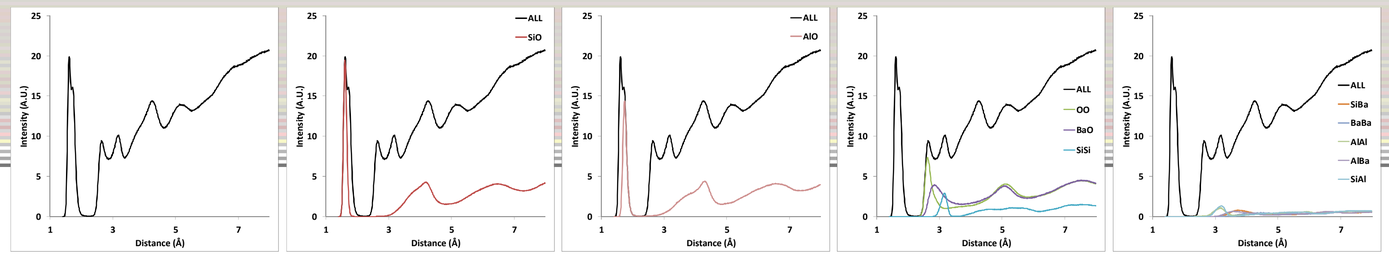
XRF of fourteen commercial sealing glasses revealed similar compositions.
Estimated compositions are comparable to literature reports.
All contained significant amounts of Barium.

Other elements can be identified for certain sealing glasses. (Zr, Pb, Zn, B, Fe, Ca, Cr, …)

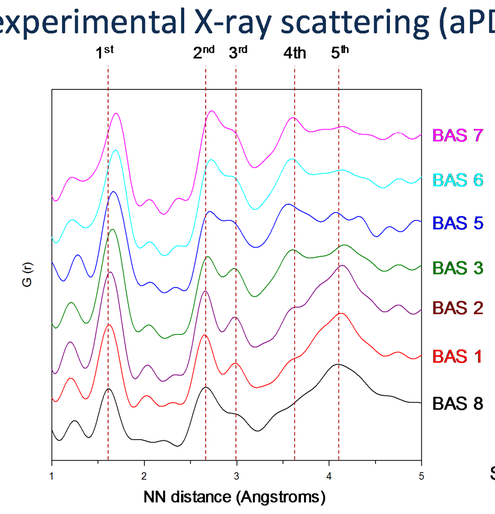
Model glass systems

	SiO_2	Al_2O_3	BaO	B_2O_3
BAS8	66.67	0	33.33	
BAS1	75	0	25	
BAS2	70	5	25	
BAS3	60	15	25	
BAS5	46	23	25	6
BAS6	42	21	25	12
BAS7	38	19	25	18





Bond-length comparisons from MD and experimental X-ray scattering (aPDF)

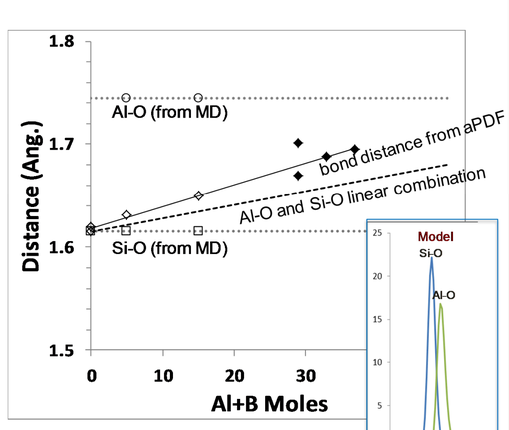


Peak identification supported by MD modeling

1st - Si-O (& Al-O)
2nd - O-Si-O
3rd - Ba-O
4th - O-Si-O-Si
5th - O-Al-O-Si-O, Ba-Ba

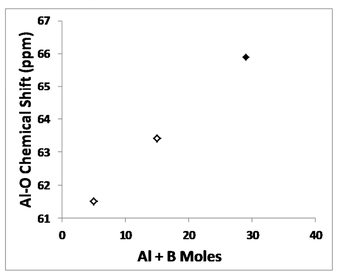
Synchrotron-based aPDF analysis (λ = 0.1430 Å; Q_{max} = 21 Å^{-1}).

Discrepancy in first nearest neighbor for aPDF and MD



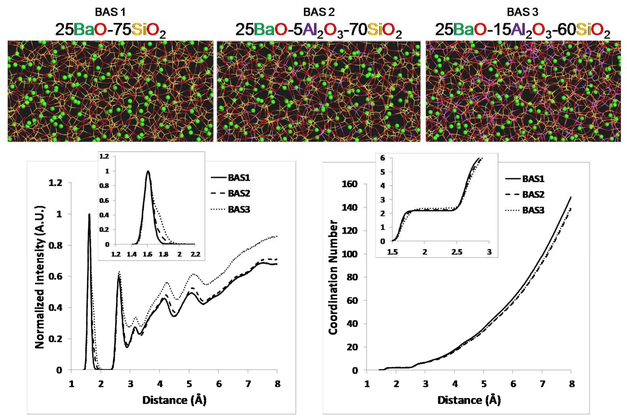
No shifts in Si NMR

^{27}Al MAS-NMR suggests that the Al-O bond length increases with Al content



Quadrupolar coupling increases with Al+B content indicating increasing local disorder.

Bond lengths and coordination number are obtained from molecular models



Chemistry-Structure relationships in BAS glasses

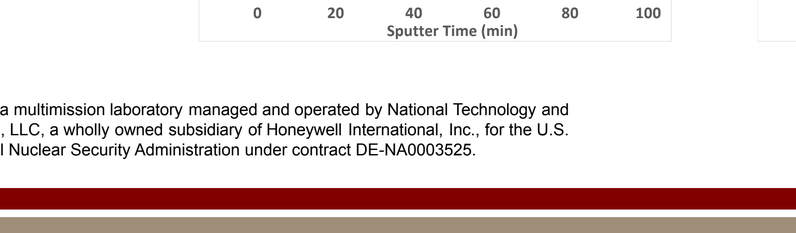
Glass	g/mole	Mole % $Al_2O_3 + B_2O_3$	NBO_{Th}	NBO_{MD}	$Connectivity_{Th}$ (BO/NF)	Archimedes Density (g/cc)	He Pycnometer Density (g/cc)	SciGlass Density (g/cc)
BAS 8	91.1	0	40.0	39.5	1.5	3.60	3.69	3.69 ± 0.01
BAS 1	83.4	0	28.6	28.0	1.67	3.29	3.32	3.31 ± 0.01
BAS 2	85.5	5	22.2	22.1	1.75	3.31	3.31	3.32 ± 0.02
BAS 3	89.7	15	10.5	13.6	1.89	3.33	3.31	3.39 ± 0.01

Peak position & symmetry increase from BAS1→ BAS2→BAS3 related to short to mid-range order

Q4/Q3 (CN) increases from BAS1→BAS2→BAS3 with decreasing non-bridging oxygens (NBO)

MD shows a long Ba-O bond length and an ill-defined coordination number.

NMR could not be used to directly interrogate Ba.

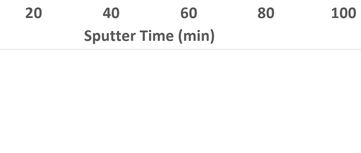


Atomic radii (pm)

O = 60 Al = 125
B = 85 Ba = 215
Si = 110

EXAFS was used to corroborate the barium local structure

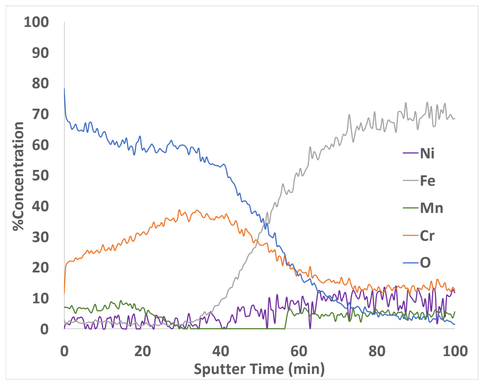
EXAFS spectrum

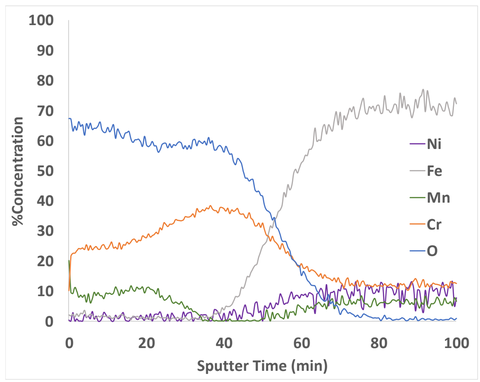


Radial distribution function

EXAFS fits were relatively insensitive to the coordination number.

Auger depth profiles of oxidized metal housings show a thick chromium oxide surface layer.





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