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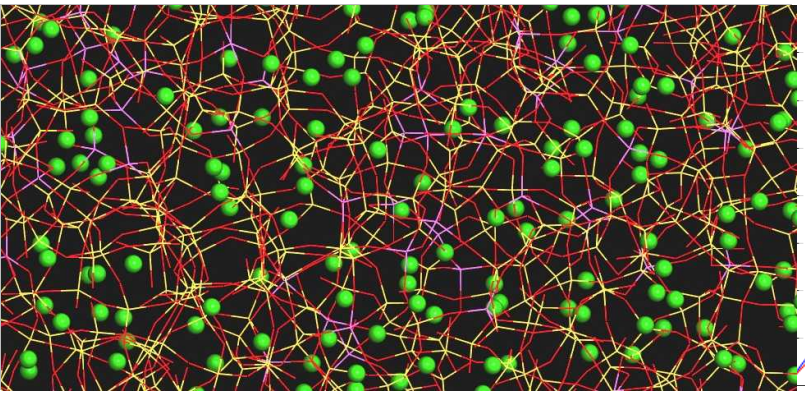

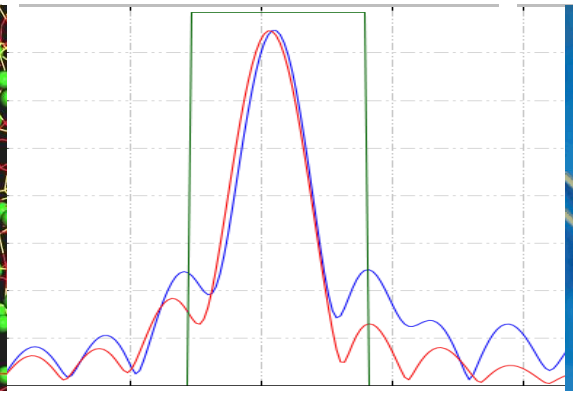

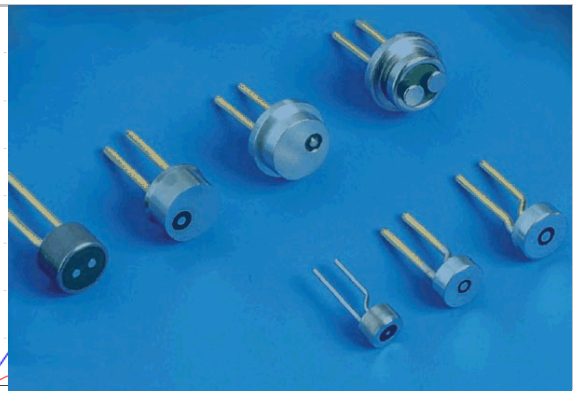

Modeling and Characterization of Exemplar Sealing Glasses to Develop Chemistry-Structure-Property Relationships

Michael Brumbach, Todd Zeitler, Todd Alam,
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U.S. DEPARTMENT OF ENERGY

National Nuclear Security Administration

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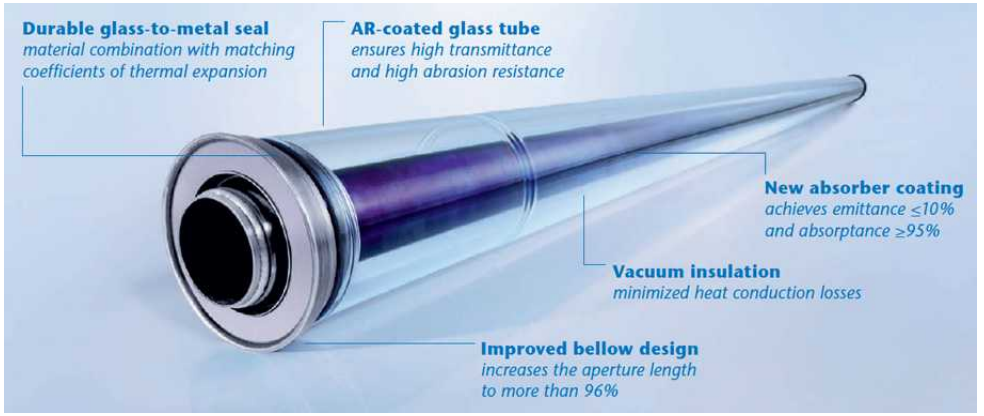
Sealing glasses are used in numerous applications

http://www.us.schott.com/epackaging/english/overview/technologies/gtms/index.html



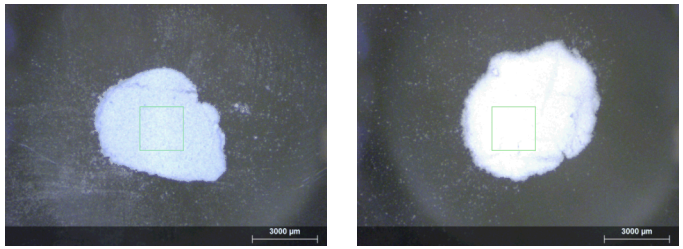
http://www.us.schott.com/csp/english/schott-solar-ptr-70-receivers.html

Glass bonded composites
- – alumina, LTCC electronic packaging

Solid oxide fuel cells (SOFC)
Concentrated solar
Glass-to-metal seals (compression seals)
- – hermetic electrical feed through
  - Medical devices

Flash lights (light bulbs)
High temperature sensor applications
Molten sodium batteries (Na/S, Na/NiCl)

Glass powder



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

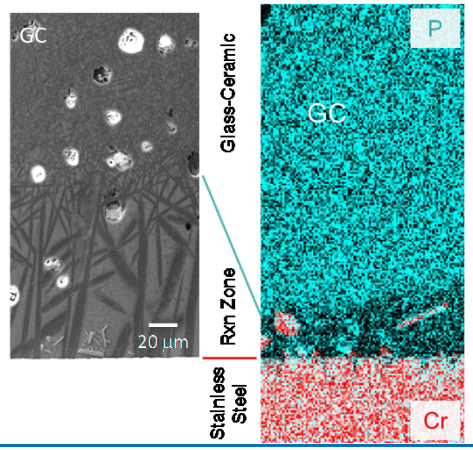
Alternatives to Glass for GtM Sealing

1) Glass-Ceramics + high CTE
+ ceramic-like properties
- complicated thermal processing to achieve microstructure

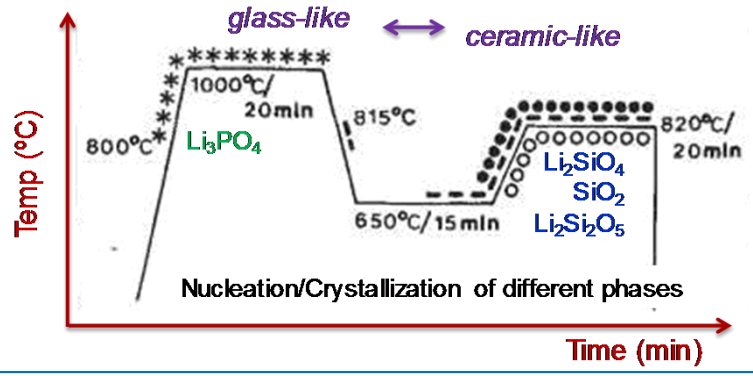
2) Filled-Glass Composites (FGCs) combine the attributes of a glass and a ceramic.

+ Glass processability
+ High/Tailorable CTE
+ Microstructural stability

Seal/Interface Is Adversely Affected By Interdiffusion & Devitrification



Glass-Ceramics - thermal processing determines microstructure)



Headley & Loehman, "Crystallization of a Glass-Ceramic by Epitaxial Growth", J Am Ceram Soc, 67 [9] 620-25 (1984).

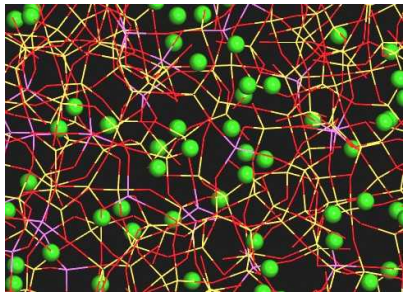
Strategy is to develop FGCs with improved processability and properties

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

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	#1	#2	#3	#4	#5	#6	#7	#8	#9	#10	#11	#12	#13	#14
	[at.%]	[at.%]	[at.%]	[at.%]	[at.%]	[at.%]	[at.%]	[at.%]	[at.%]	[at.%]	[at.%]	[at.%]	[at.%]	[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**

Molecular dynamic calculations have been performed on the model BAS glass formulation

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BAS Glasses Were Simulated With The LAMMPS** MD Code & Pedone* Multicomponent Force Field

Glass	Oxide Mole %			Archimedes Density (g/cc)	Number of Atoms (in 1x/4x Simulation)					Box Length (Å)
	BaO	Al_2O_3	SiO_2		Ba	Al	Si	O	Total	
BAS 1	25		75	3.52	275/ 1100	0/ 0	825/ 3300	1925/ 7700	3025/ 12100	35.108/ 55.731
BAS 2	25	5	70	3.25	275/ 1100	110/ 440	770/ 3380	1980/ 720	3125/ 12540	36.354/ 57.709
BAS 3	25	15	60	3.22	275/ 1100	330/ 1320	660/ 2640	2090/ 8360	3355/ 13420	37.053/ 58.818

A Pedone et al., "A new self-consistent empirical interatomic potential model for oxides, silicates, and silica-based glasses", J Phys Chem B, **110, 11780-11795 (2006).*

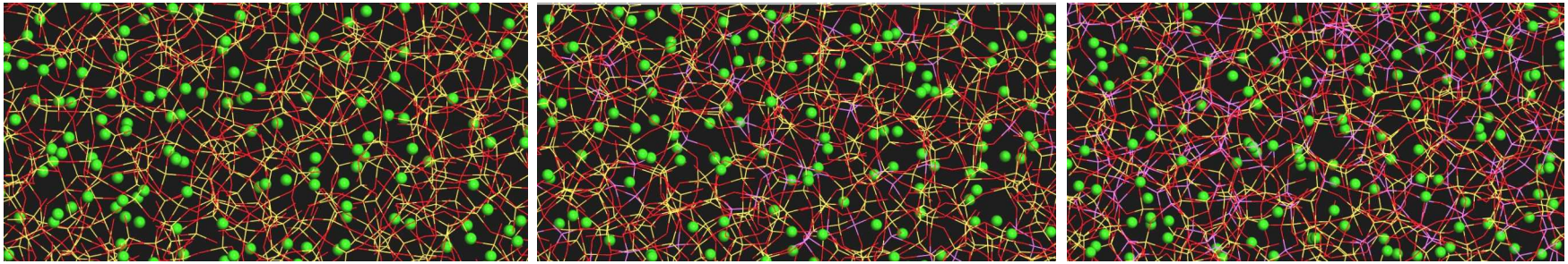
***S Plimpton, "Fast Parallel Algorithms for Short-Range Molecular-Dynamics, J Comp Phys, **117** [1], 1-19 (1995).*

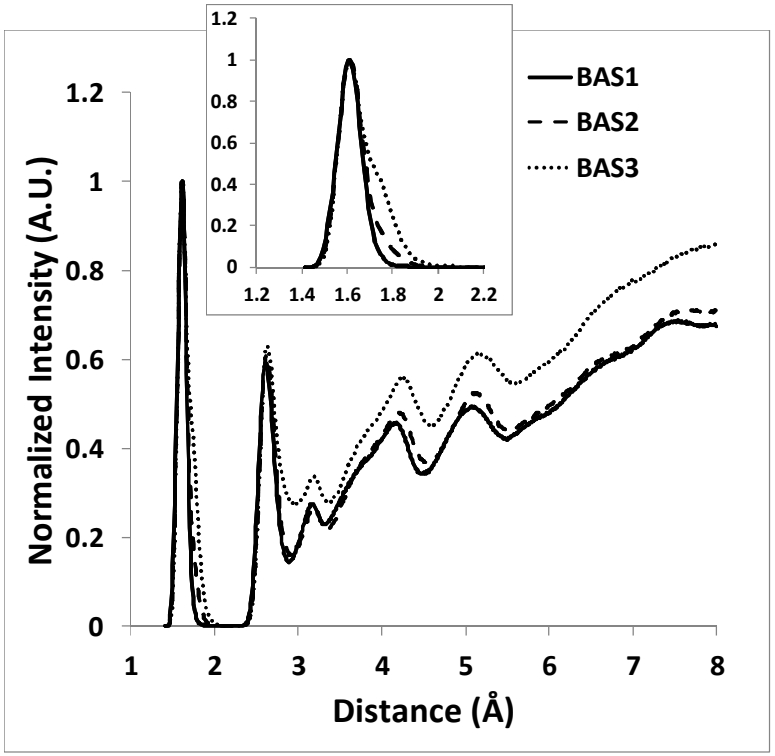
Bond lengths and coordination number are obtained from molecular models

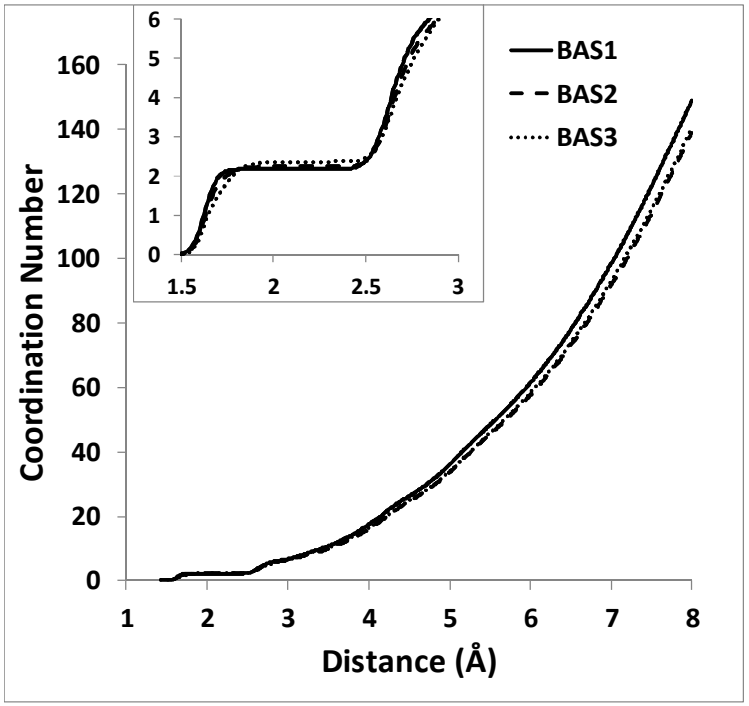
BAS 1
$25BaO\text{-}75SiO_2$

BAS 2
$25BaO\text{-}5Al_2O_3\text{-}70SiO_2$

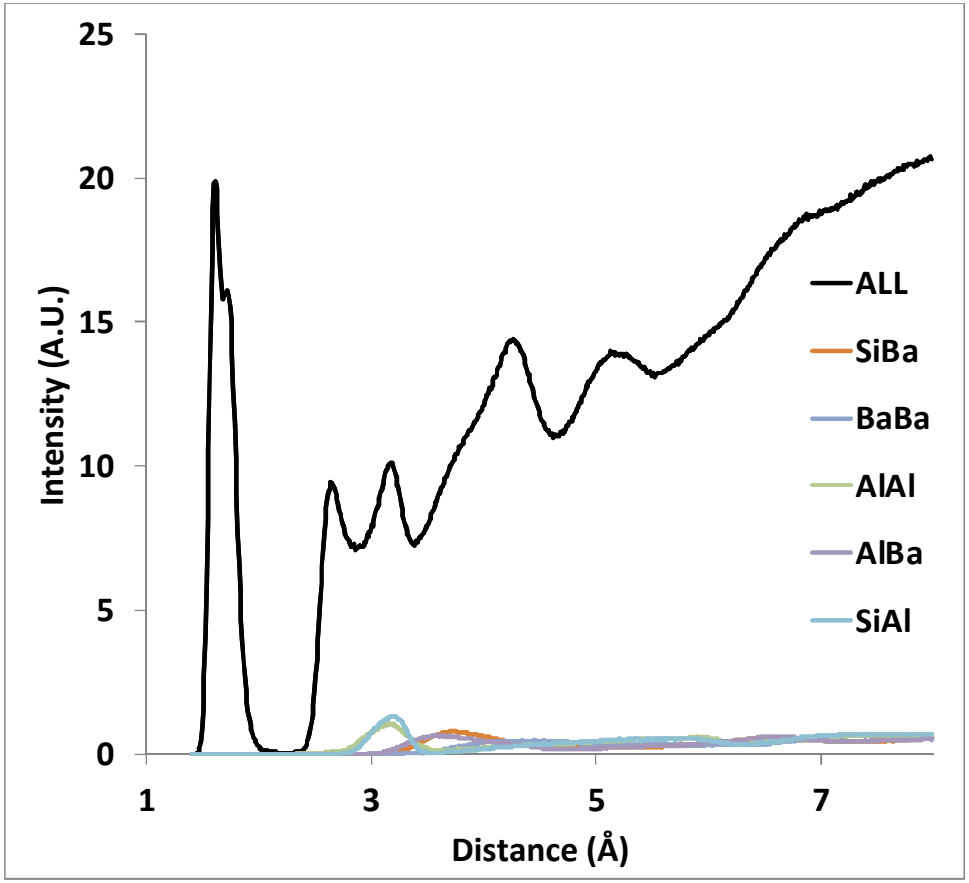
BAS 3
$25BaO\text{-}15Al_2O_3\text{-}60SiO_2$



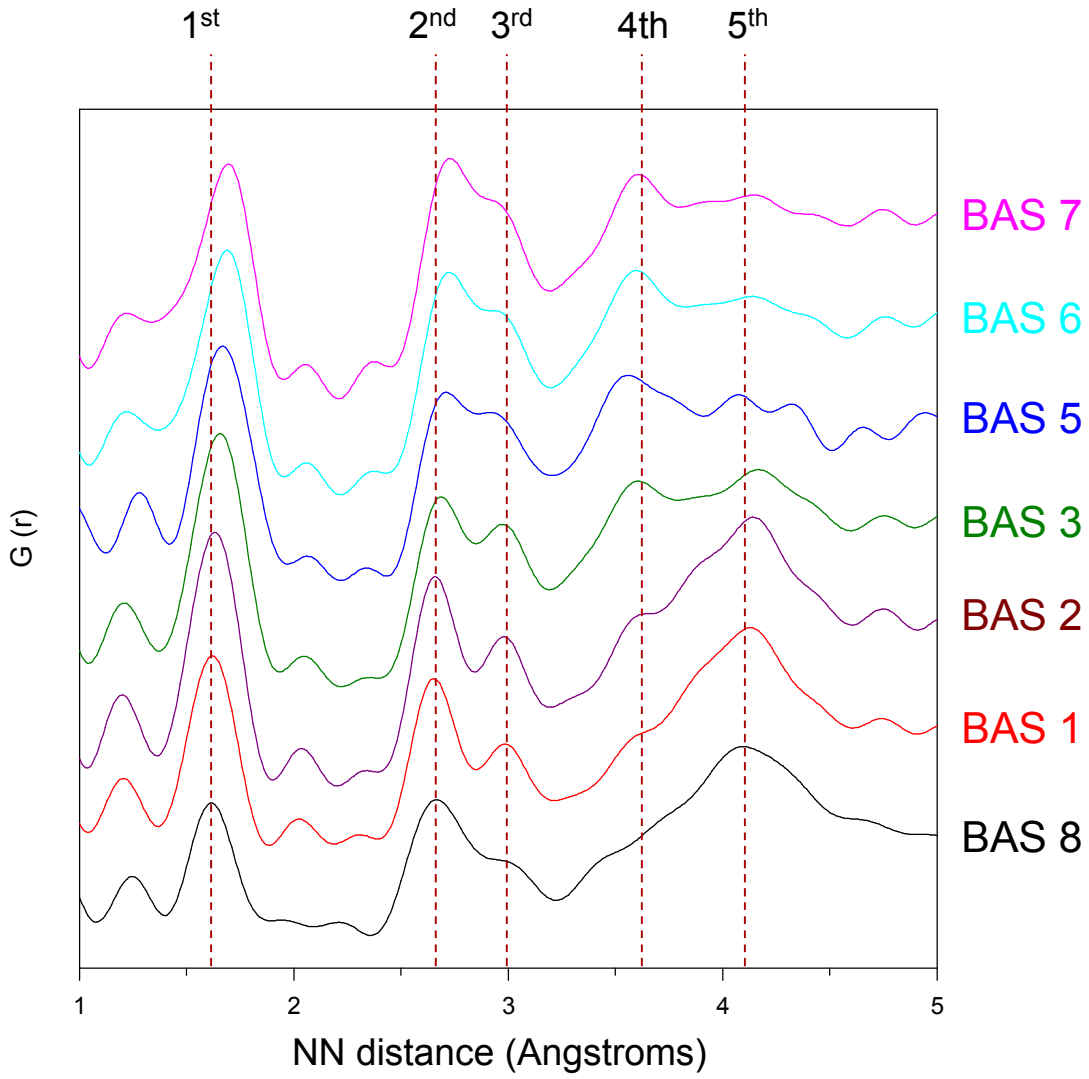




Molecular dynamics shows specific bonds with high resolution



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

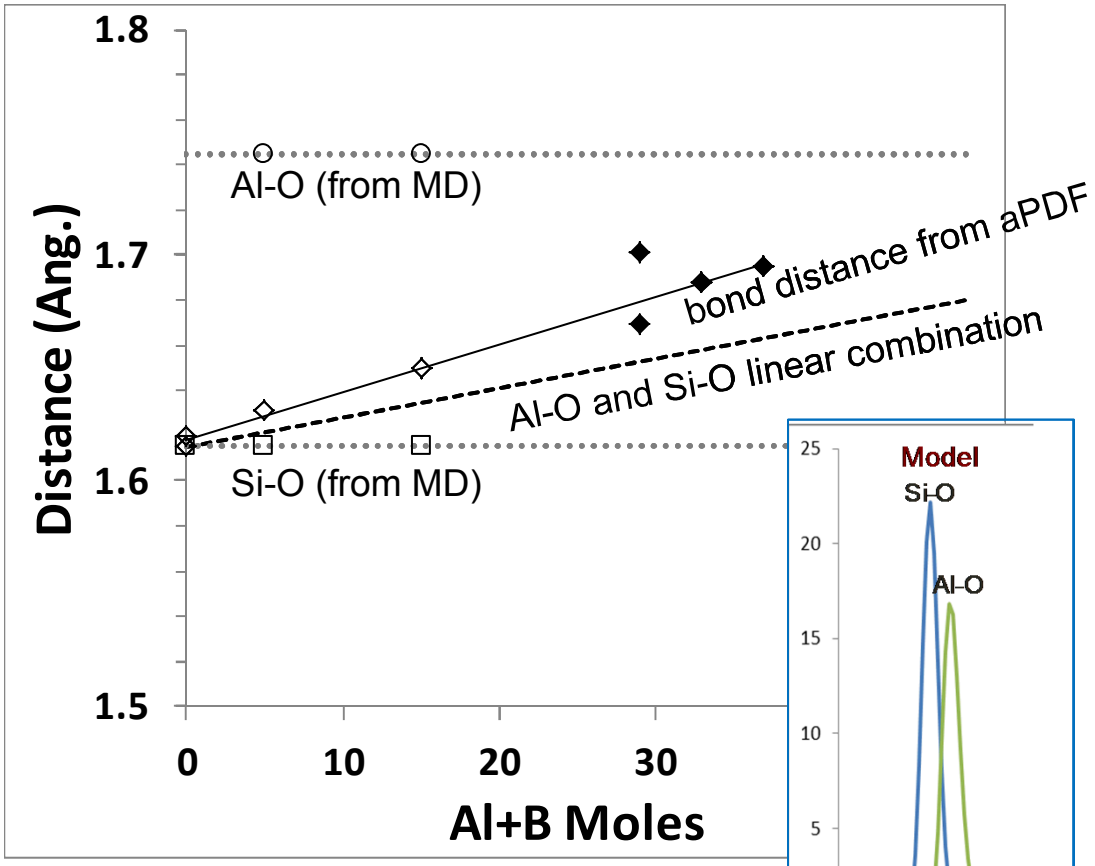


Peak identification supported by MD modeling

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

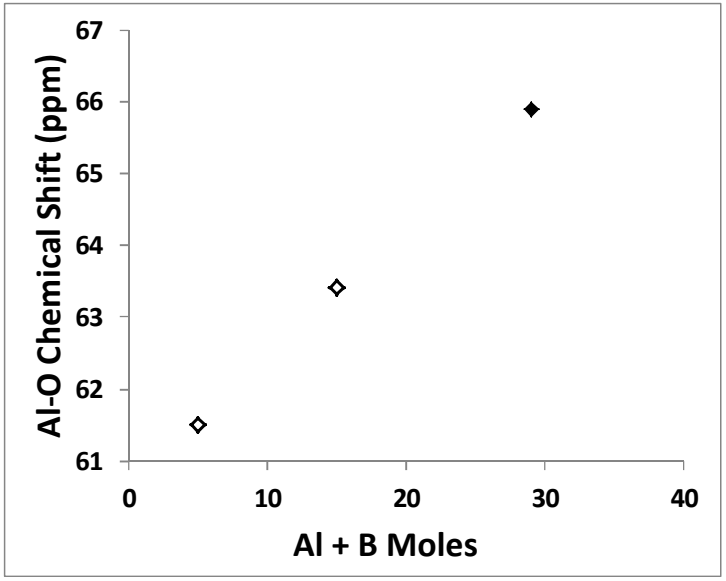
Synchrotron-based aPDF analysis (λ = 0.1430 Å; Q_{max} = 21 Å^{-1}).

Discrepancy in first nearest neighbor for aPDF and MD



No shifts in Si NMR

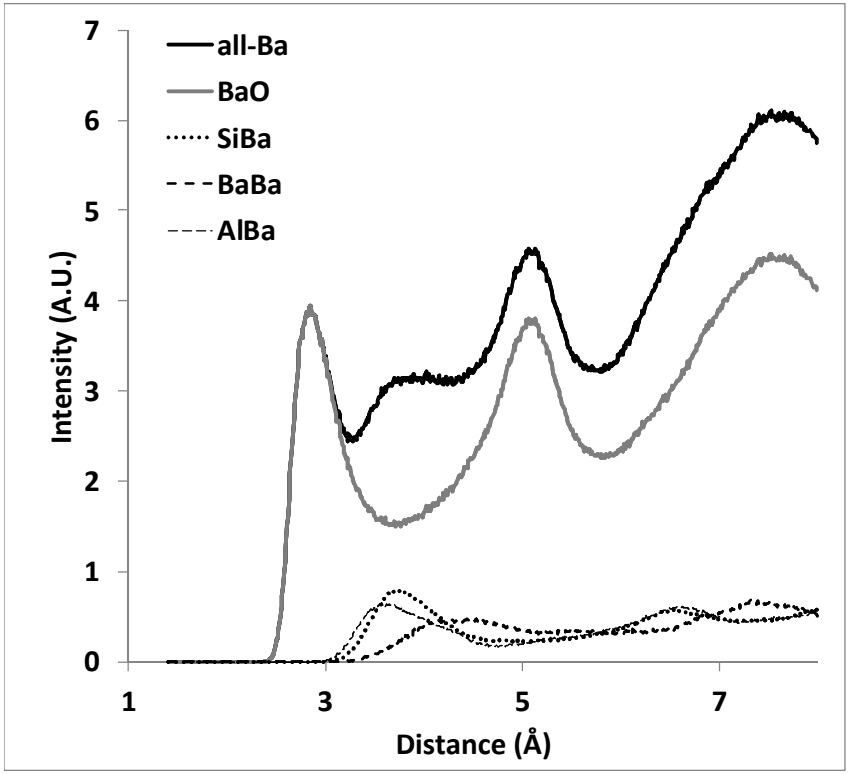
^{27}Al MAS-NMR suggests that the Al-O bond length increases with Al content

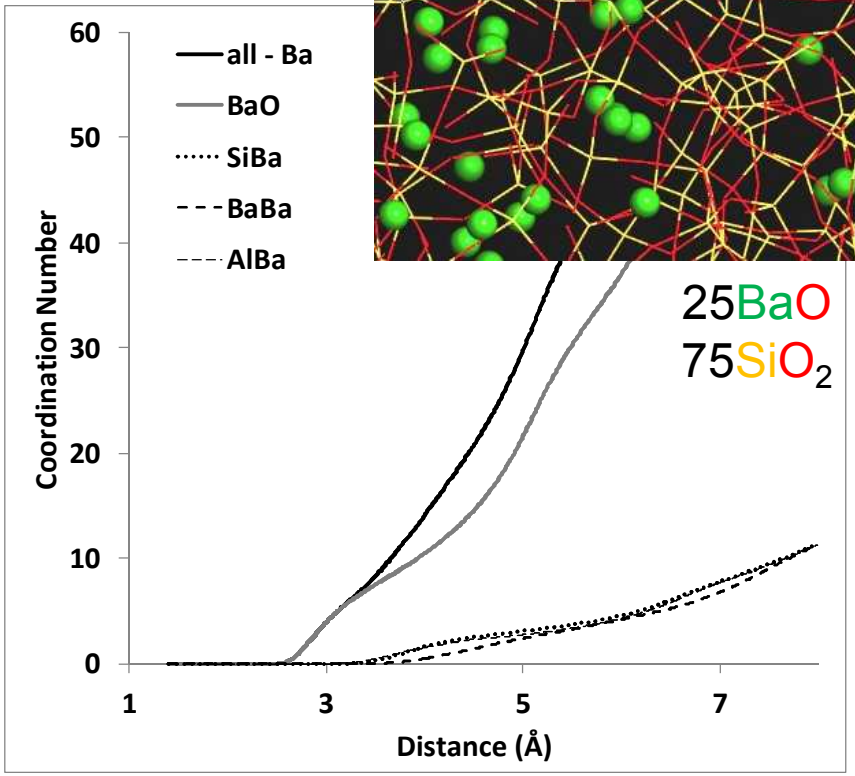


Quadrupolar coupling increases with Al+B content indicating increasing local disorder.

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

NMR could not be used to directly interrogate Ba.





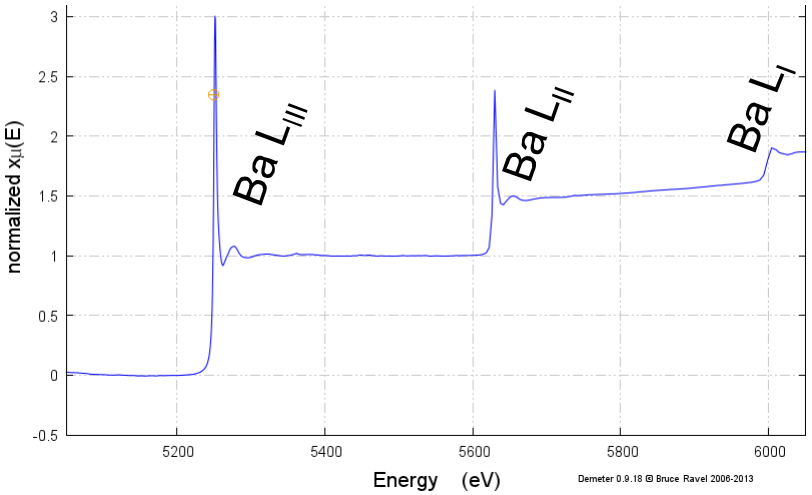
Atomic radii (pm)

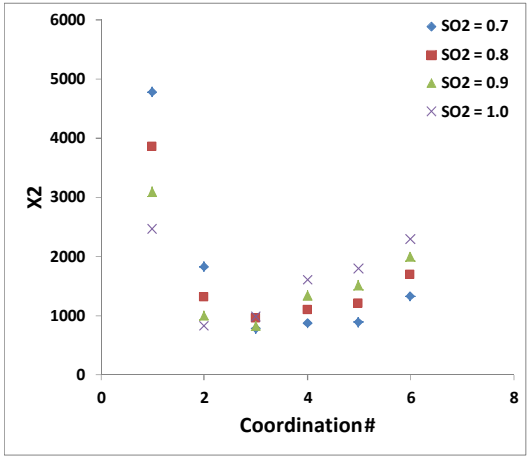
O = 60	Al = 125
B = 85	Ba = 215
Si = 110	

EXAFS was used to corroborate the barium local structure

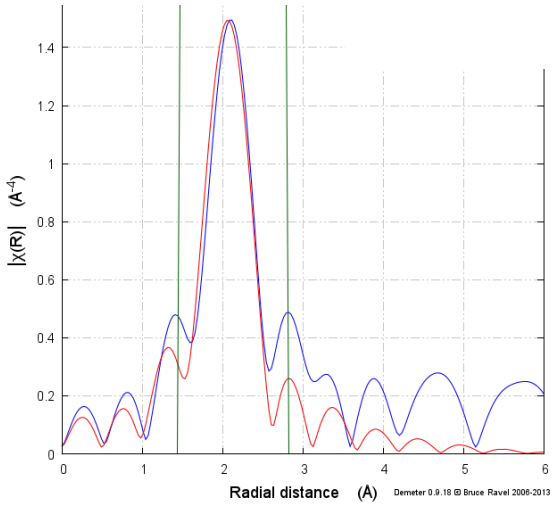
EXAFS fits were relatively insensitive to the coordination number.

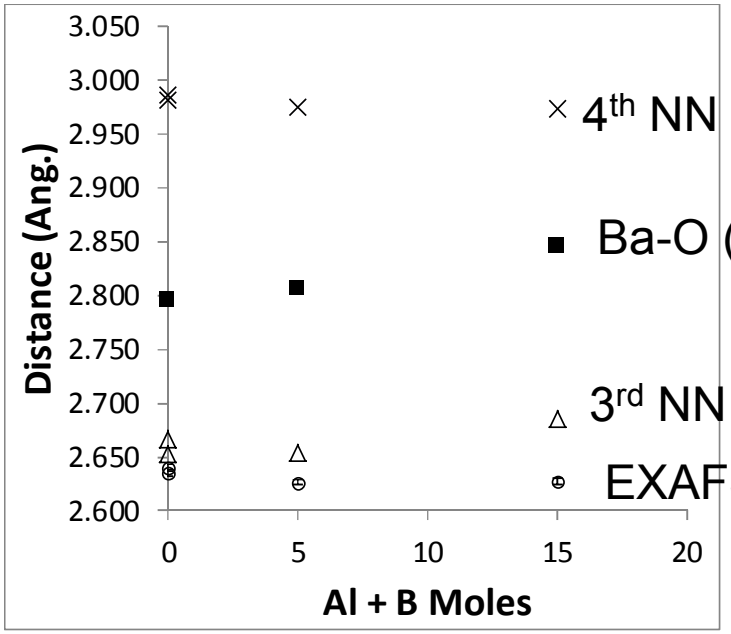
EXAFS spectrum



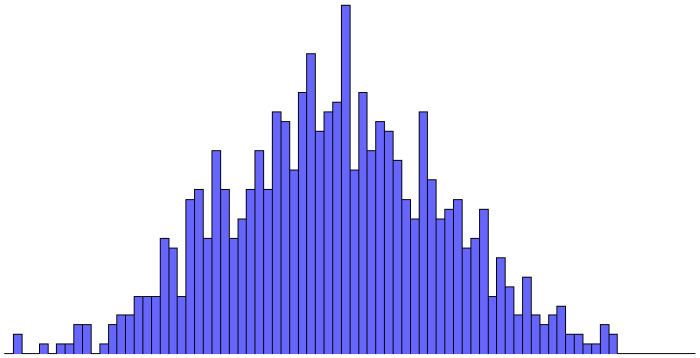


Radial distribution function

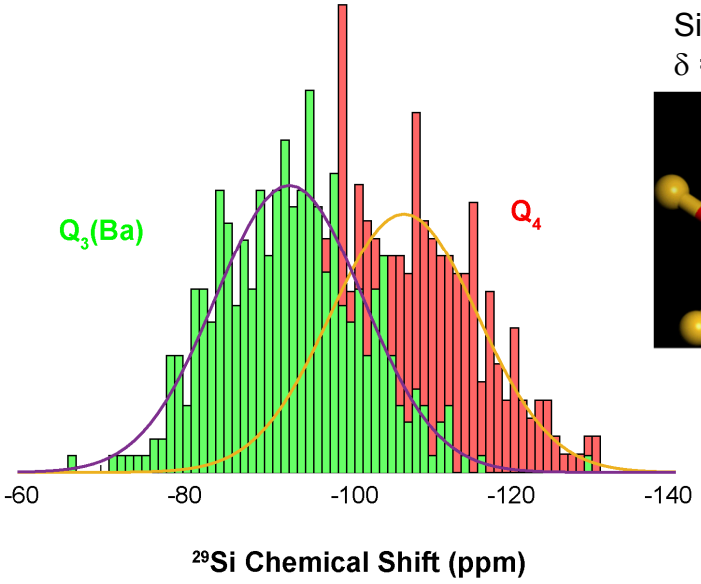




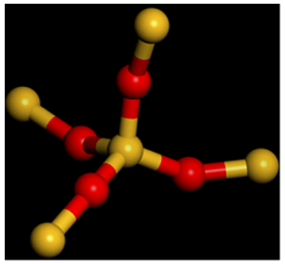
^{29}Si MAS-NMR peak-shifts can be predicted from MD coordinates



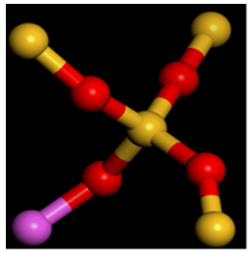
bond valence (s_i)
angle of the bridging oxygen
Si-O bond distance
distance to Si 2nd nearest neighbors



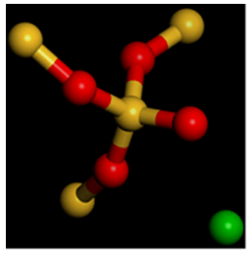
$Si(OSi)_4$
δ = -102.1 ppm



$Si(OSi)_3Al$
δ = -74.4 ppm



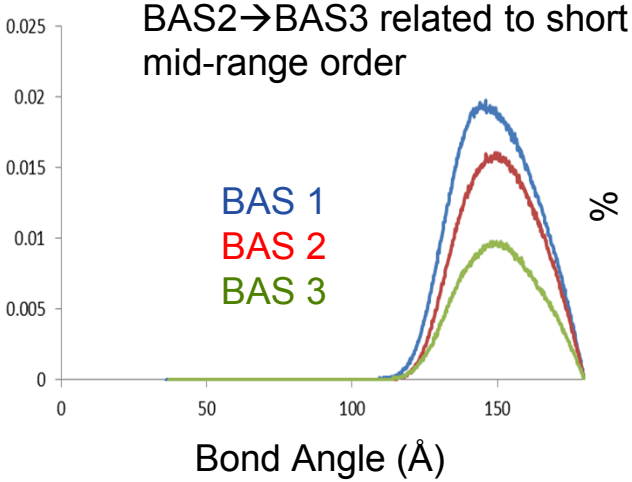
$Si(OSi)_3Ba$
δ = -92.5 ppm



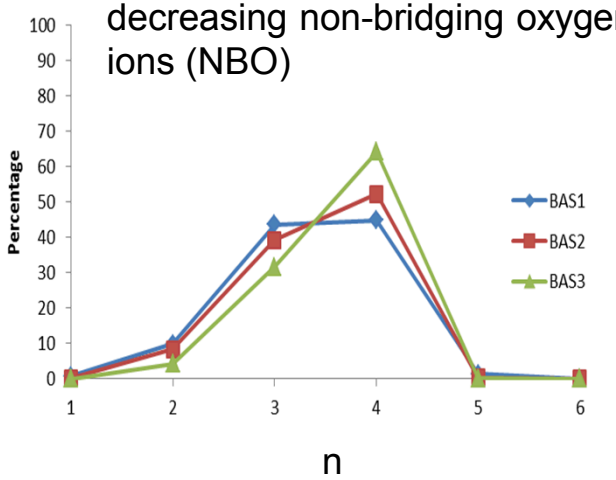
Chemistry-Structure relationships in BAS glasses

Glass	g/mole	Mole % Al_2O_3 + B_2O_3	NBO_{Th}	NBO_{MD}	$Connectivity_{Th}$ (BO/NF)	Archi-medes 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 oxygen ions (NBO)



Structure-Property relationships informed from modeling and experiment.

Glass	Measured T_g (°C)	Model T_g (°C)	Measured C_p (J/g K) @35 °C	Model C_p (J/g K)	Measured CTE (in/in/°C)	Model CTE Below Tg (in/in/°C)	Model CTE Above Tg (in/in/°C)
BAS 8	---	1532 ± 75	0.636	0.763 ± 0.006		14.4 ± 0.9	35.7 ± 2.4
BAS 1	---	1473 ± 95	---	0.858 ± 0.004		11.6 ± 0.5	31.0 ± 6.3
BAS 2	780	1365 ± 225	0.635	0.867 ± 0.004		10.4 ± 0.6	24.1 ± 6.1
BAS 3	751	1394 ± 116	0.619	0.884 ± 0.004		10.1 ± 0.4	19.1 ± 4.2

CTE decreases with increasing connectivity induced by added alumina.

c_p values increase with increasing alumina.

Glasses can be readily simulated to evaluate chemistry-structure-property relationships

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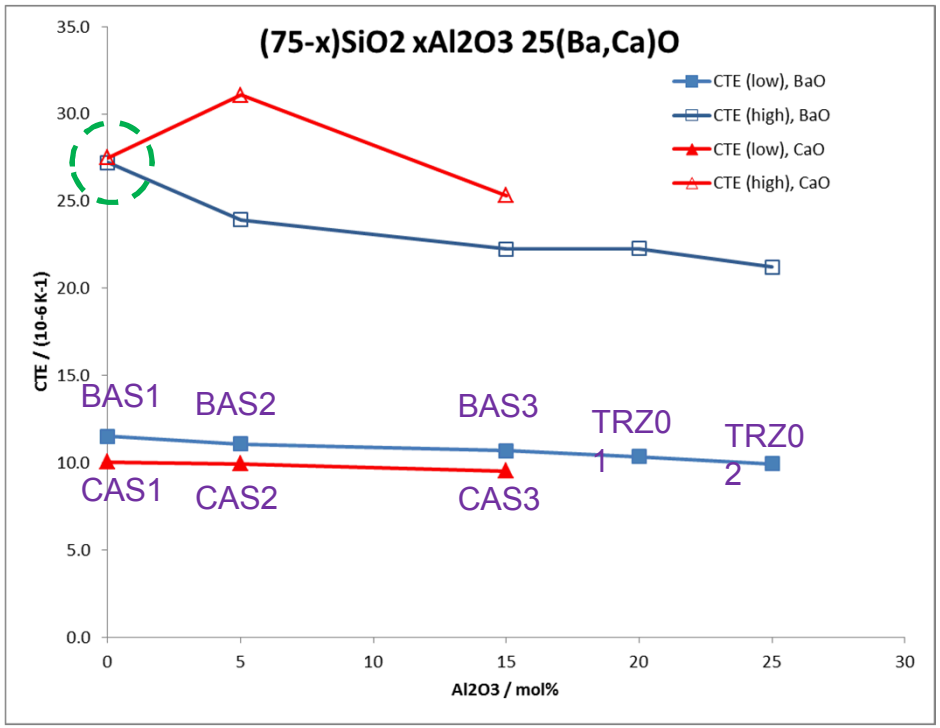
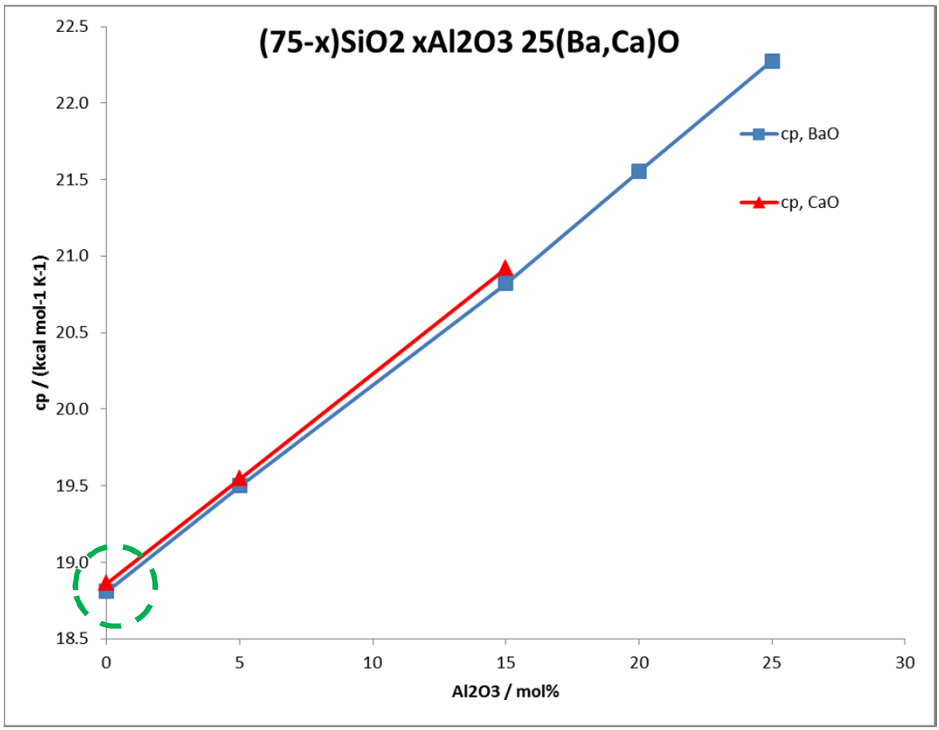
	mol%							# atoms	from Priven-2000 (SciGlass)	from our experiments	Results (SciGlass Densities)											
Glass Name	SiO_2	Al_2O_3	BaO	CaO	B_2O_3	Na_2O	K_2O	Total	density (g/cm^3)	density (g/cm^3)	density (g/cm^3)	±	α_L ($10^{-6} K^{-1}$) (low)	±	α_L ($10^{-6} K^{-1}$) (high)	±	T_g (K)	±	c_p (kcal $mol^{-1} K^{-1}$)	±	c_p ($J\ g^{-1} K^{-1}$)	±
BAS1	75	0	25					3025	3.294	3.52	3.30	0.01	11.5	0.7	27.2	3.0	1603	93	18.8	0.1	0.858	0.004
BAS2	70	5	25					3135	3.314	3.25	3.33	0.00	11.1	0.4	23.9	5.0	1709	165	19.5	0.1	0.868	0.002
BAS3	60	15	25					3355	3.330	3.22	3.39	0.01	10.7	0.2	22.3	7.1	1695	83	20.8	0.1	0.883	0.005
BAS8	66.7		33.3					3000	3.685		3.60	0.01	14.4	0.9	35.7	2.4	1532	75	18.8	0.1	0.763	0.006
CAS1	75	0		25				3025	2.512		2.57	0.01	10.0	0.8	27.5	7.2	1710	106	18.9	0.1	0.860	0.005
CAS2	70	5		25				3135	2.544		2.64	0.01	9.9	0.4	31.1	11.9	1670	147	19.5	0.1	1.215	0.006
CAS3	60	15		25				3355	2.586		2.77	0.01	9.5	1.1	25.3	5.5	1627	48	20.9	0.1	1.217	0.008
CAS8	66.7			33.3				3000	2.626		2.64	0.01	12.4	0.6	35.7	6.3	1528	175	18.8	0.1	1.191	0.006
TRZ01	55	20	25					3465	3.318		3.45	0.01	10.4	0.4	22.3	2.1	1632	74	21.6	0.2	0.893	0.008
TRZ02	50	25	25					3575	3.307		3.48	0.02	9.9	0.3	21.2	4.0	1512	263	22.3	0.1	0.903	0.004
Cor9013Na	70	3.5	12			14.5		3540	2.892		2.90	0.02	15.3	0.7	35.2	4.3	1427	153	22.4	0.1	1.070	0.005
Cor9013K	70	3.5	12				14.5	3540	2.860		2.77	0.02	18.8	0.6	40.4	13.4	1502	273	22.4	0.1	1.023	0.004
PC1	50		10			40		3190	2.990		2.95	0.01	27.5	0.6	65.3	0.6	786	17	22.2	0.2	1.205	0.010
PC2	50		30			20		2970	3.762		3.61	0.01	21.7	0.7	51.7	0.7	866	17	19.7	0.1	0.847	0.006
TRZ03	50		20			30		3080	3.393		3.29	0.01	25.6	0.9	58.2	0.3	838	16	20.9	0.2	1.005	0.008
TRZ04	50		10			10	30	3190	2.907		2.85	0.01	35.4	2.6	83.9	0.3	754	16	23.0	0.1	1.095	0.007
TRZ05	50		10			20	20	3190	2.932		2.89	0.00	31.7	1.2	78.2	0.5	739	11	22.9	0.2	1.135	0.009
TRZ06	50		10			30	10	3190	2.959		2.92	0.01	30.6	0.8	72.1	0.6	770	29	22.6	0.2	1.173	0.011
TRZ07	50	10	10				30	3410	2.897		2.78	0.02	33.1	0.7	69.5	10.7	1494	141	22.6	0.2	1.024	0.010
TRZ11	50	10	10			30		3410	2.968		2.94	0.01	21.8	0.7	43.5	0.7	1057	70	22.3	0.1	1.145	0.007

Simulated glasses can reveal differences in expected properties



CAS glasses have lower CTEs below T_g, and higher CTEs above T_g



BAS & CAS Glass C_p increases with increasing Al_20_3 Content

BAS 2

25 BaO - 5 Al_2O_3 - 70 SiO_2

CAS 2

25 CaO - 15 Al_2O_3 - 60 SiO_2

Conclusions

- Based upon commercial sealing glass compositions, simple 3-component glasses were synthesized.
- Molecular dynamics models and experimental characterization were performed on the three component glasses.
- MD simulations and experiment inform structural characterization.
  - MD informs peak assignments in aPDF.
  - MD implicates a need for higher resolution in aPDF, however, MAS-NMR suggests a change in bond-length not captured by MD.
  - Barium local coordination environment is ill-defined, as demonstrated by EXAFS and MD, and leads to non-bridging oxygens.
  - Aluminum increases glass connectivity leading to lower CTE.
- MD and experiment show agreement on glass density.
- Trends in thermal properties need more experimental data for validation, but modeling can suggest directions for glass composition.

NMR suggests significant changes in B-O with glass chemistry. MD for B is being developed.

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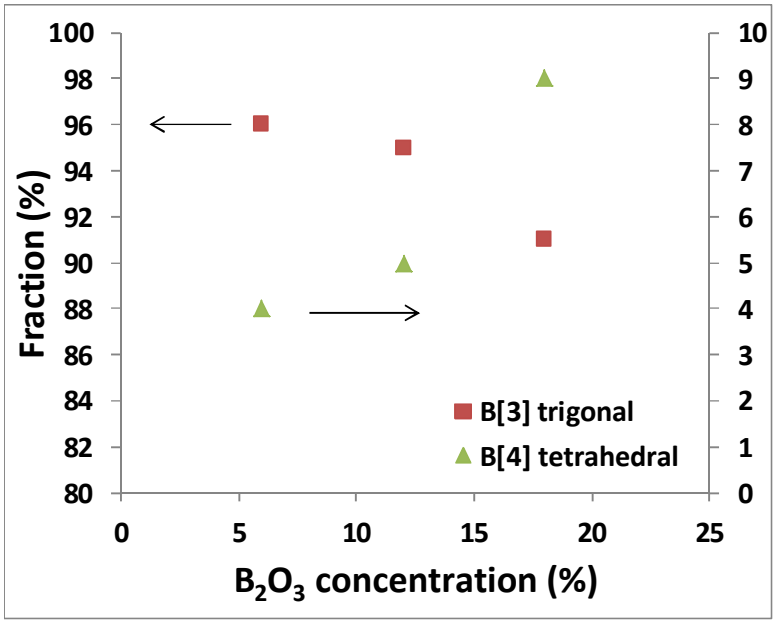
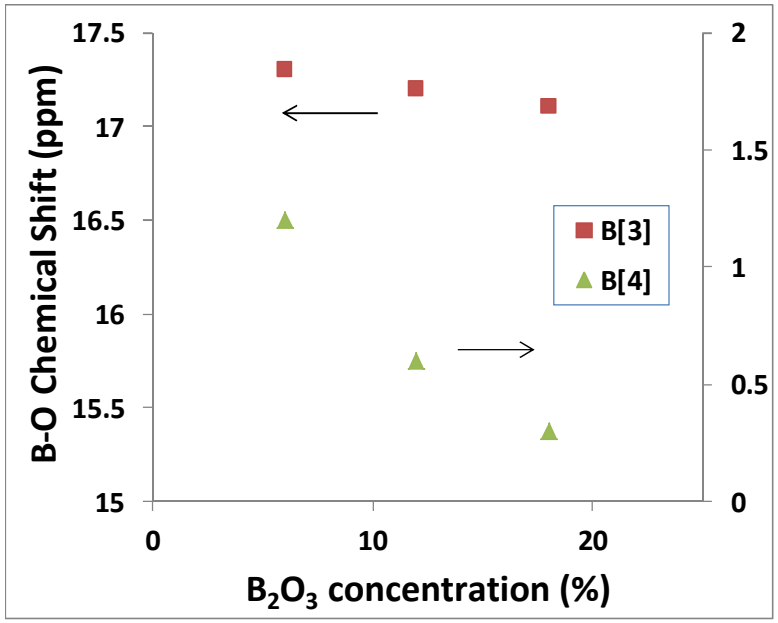
^{11}B MAS-NMR - boron speciation becomes more tetrahedral with increasing B content



^{11}B MAS-NMR shows that B-O bond length decreases with B content



Barium structure