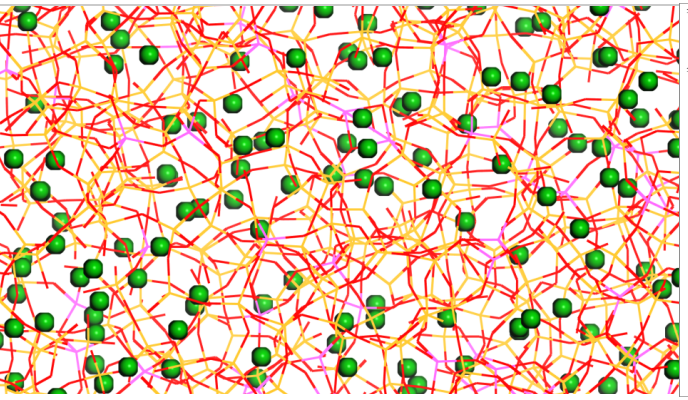
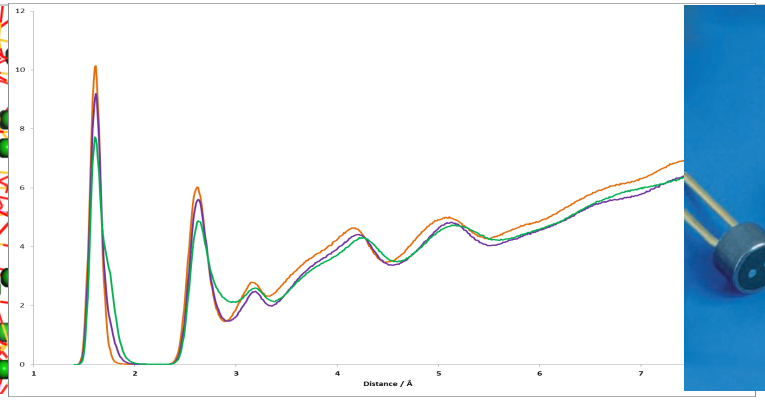
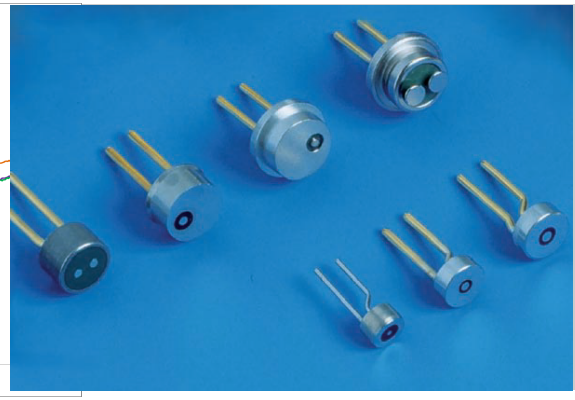
Exceptional service in the national interest

SAND2015-4655C

1:30 – 2:00 PM
Session: Advanced Powder Processing to Develop Ceramics & Composites
Symposium: T4S4 - Powder Processing Technology for Advanced Ceramics







Characterization & Modeling of Glass Chemistry-Structure-Property Relations To Develop Advanced Glass Composites

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The 11th International Conference on Ceramic Materials and Components for Energy and Environmental Applications (CMCEE 11)
Vancouver, British Columbia , Canada

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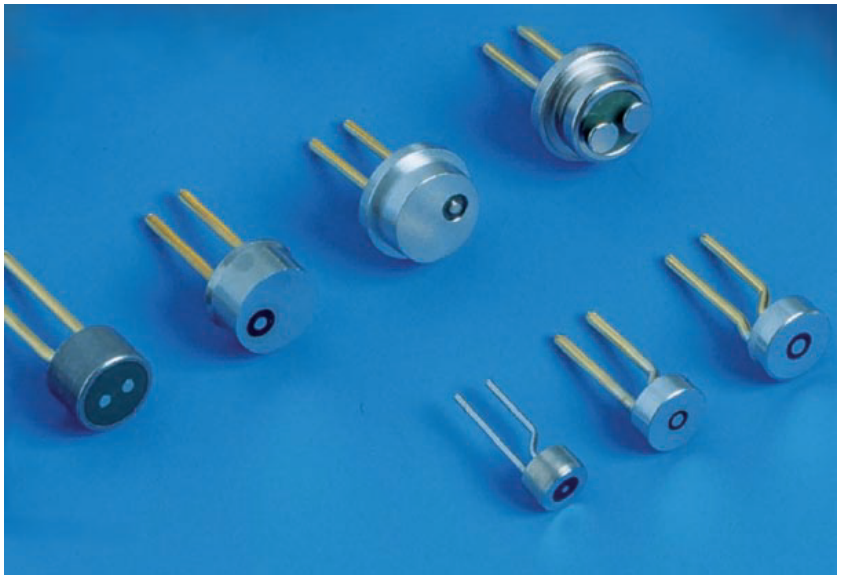
Glass Is Used To Bond/Join Materials

- **Glass bonding/joining Applications**
  - Glass-bonded composites
    - Glass-bonded alumina
    - Low temperature co-fired ceramic (LTCC) electronic packaging
  - Seals
    - Hermetic glass to metal (GtM) seals
      - Air bags “motors”
      - Medical implants
      - Microelectronics
    - Energy conversion
      - Solid oxide fuel cells (SOFCs)
      - Concentrated solar

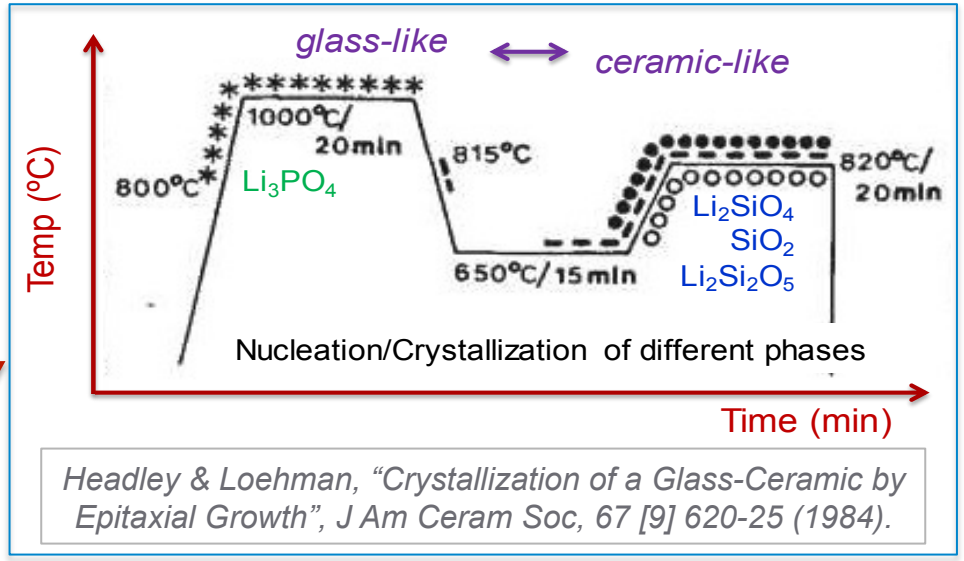


Filled Glass Composites (FGCs) Have The Processability of a Glass and the Properties of A Ceramic

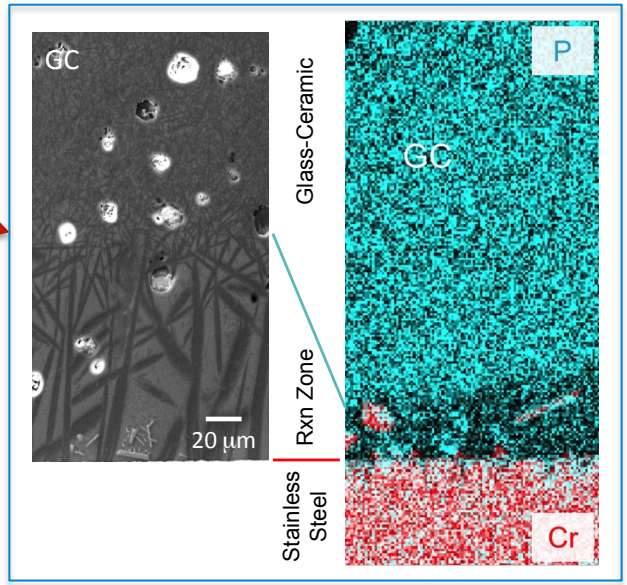
Glass
+ Processability
+ Materials Compatibility
- Low/fixed CTE
- Low toughness/crack tolerance

Glass-Ceramic (GC)
+ Toughness/crack tolerance
+ High/Tunable CTE
- Process sensitivity
- Reactivity/Instability

Filled Glass Composite (FGC)
+ Process Robustness
+ Toughness/crack tolerance
+ Low to High/Tunable CTE
+ Chemical/structural stability

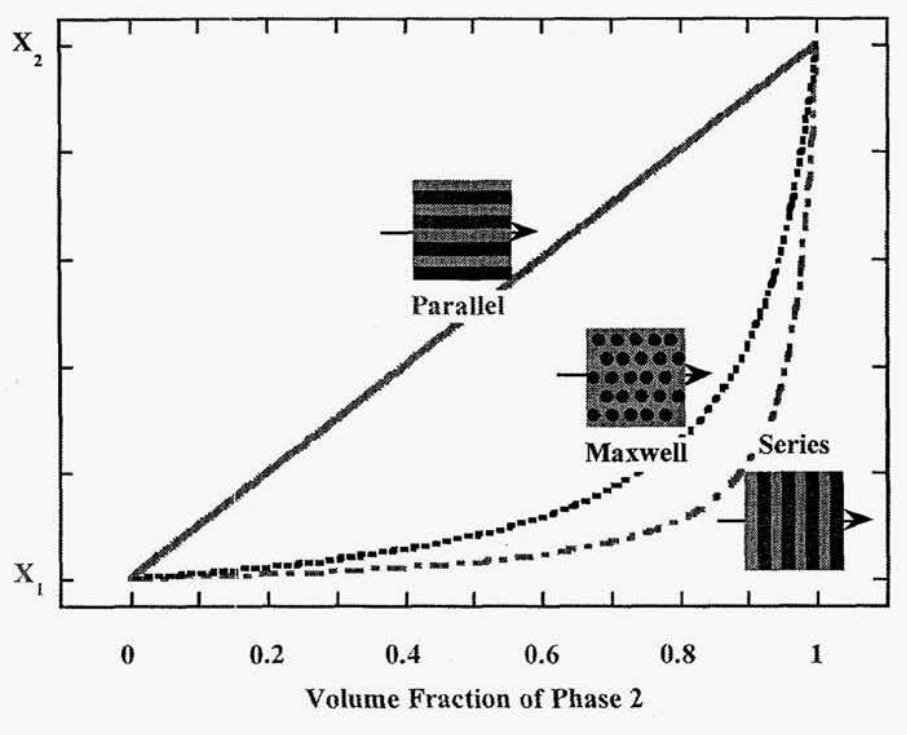


Headley & Loehman, "Crystallization of a Glass-Ceramic by Epitaxial Growth", J Am Ceram Soc, 67 [9] 620-25 (1984).



Composite Process & Property Models Are Availble To Design Manufacturable, Tailored-Property FGCs

Validated FGC Property Models

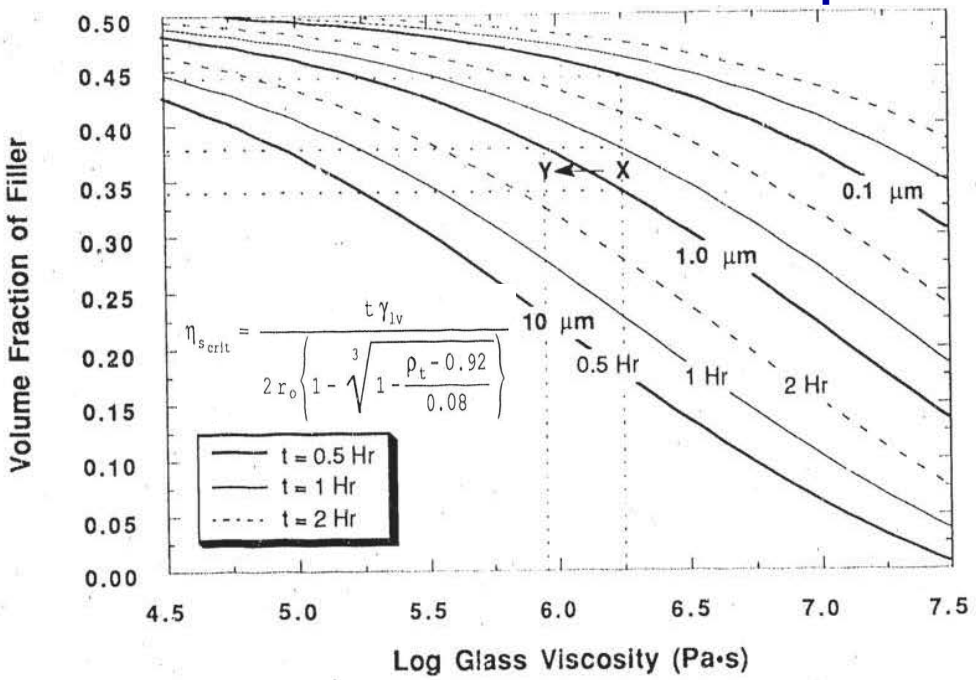


Ewsuk & Harrison, Trans ACerS, 1995

Euler's Model

$$\eta_s = \eta \left(1 + \frac{\kappa \phi}{1 - \left(\phi / \phi_{max}\right)}\right)^2$$

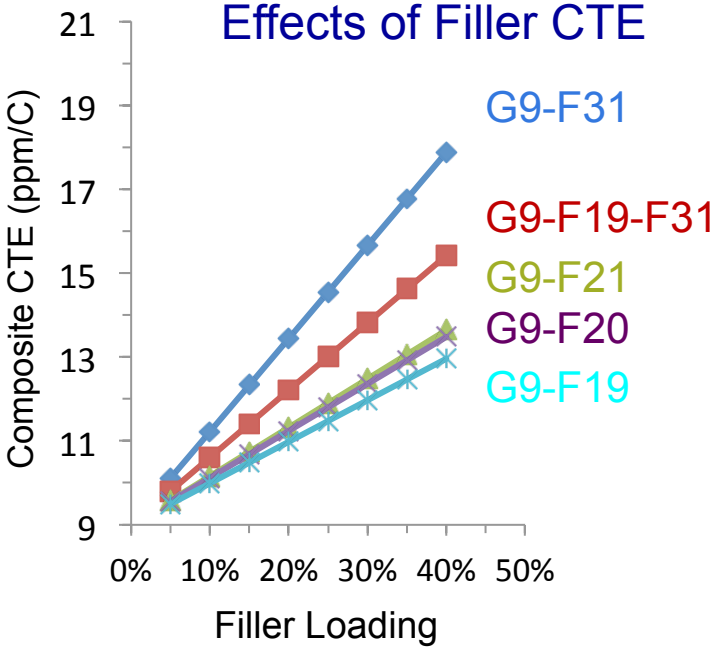
FGC Process Models & Maps



Ewsuk & Harrison, Ceramic Trans, 1995

FGC Processability and Properties Can Be Tuned

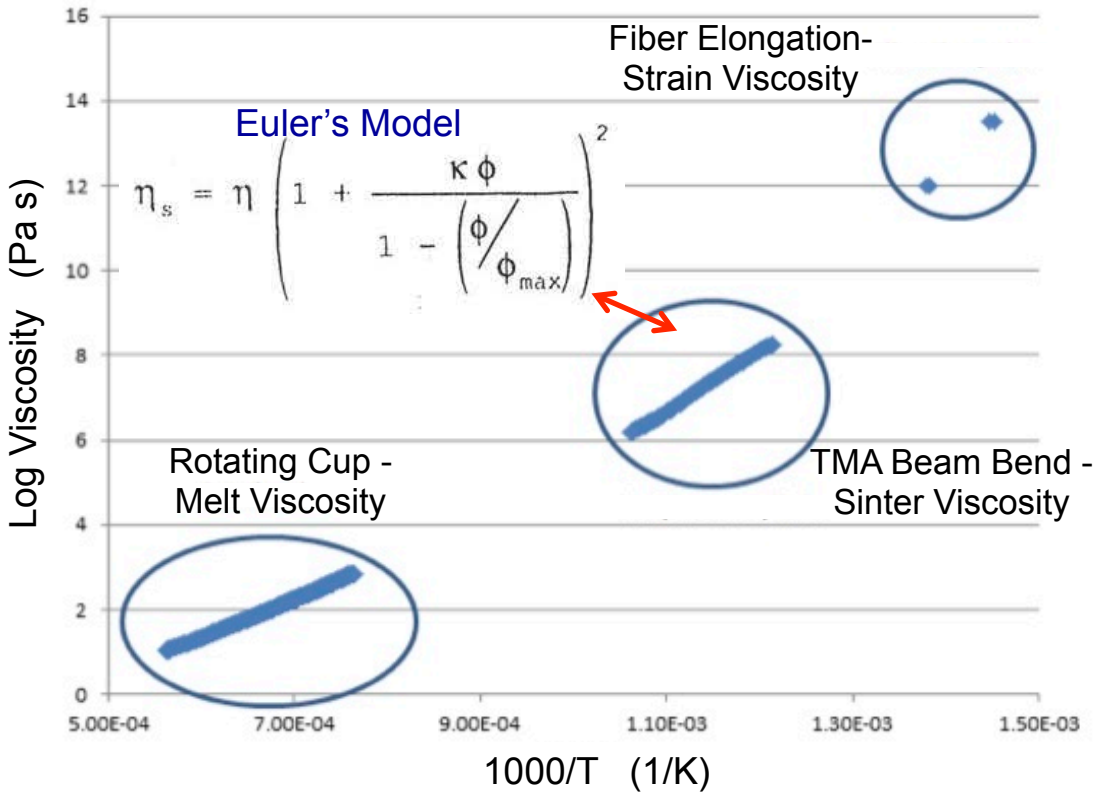
Effects of Filler CTE



FGC CTE is tuned by controlling filler CTE and the filler loading

2.5 cm diameter 10 vol% filled glass composite

BAS Matrix Glass Viscosity



FGC viscosity is tuned by controlling filler loading and glass viscosity

Composite Design Is Being Augmented With Modeling To Understand Glass Chemistry-Structure Relations

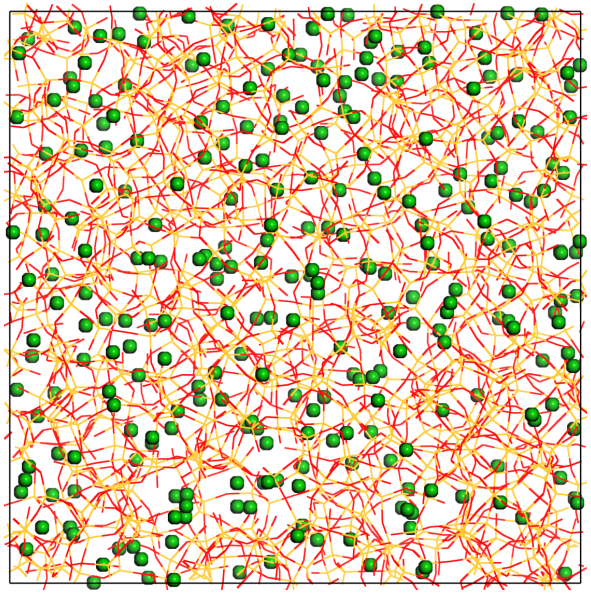
- **Approach**
  - Develop experimentally-validated modeling/simulation tools to predict/control glass chemistry-structure-property relations.
- **Tasks**
  - Characterize & model glass chemistry-structure-property relations
    - In a simple/model 3-component glass
    - In more complex 6-7 component glasses
  - Test, refine, & validate modeling/simulation by comparison to experiment
- **Future Work**
  - Characterize & model glass chemistry-structure-property relations at Interfaces
  - Design/Fabricate & characterize filled-glass composite microstructure and properties

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

25 BaO – X Al_2O_3 – (75-x) SiO_2 Glasses

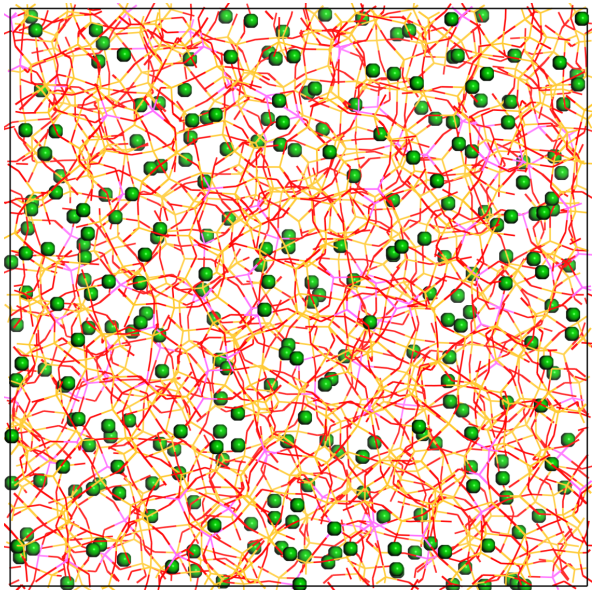
BAS 1

25 BaO - 75 SiO_2



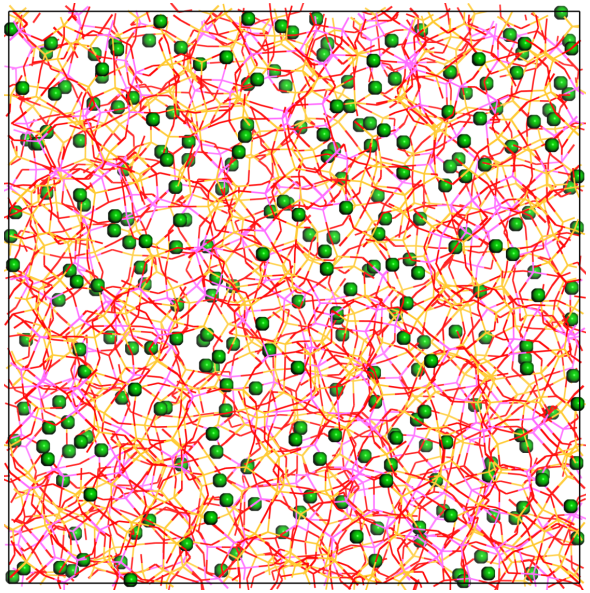
BAS 2

25 BaO - 5 Al_2O_3 - 70 SiO_2



BAS 3

25 BaO - 15 Al_2O_3 - 60 SiO_2



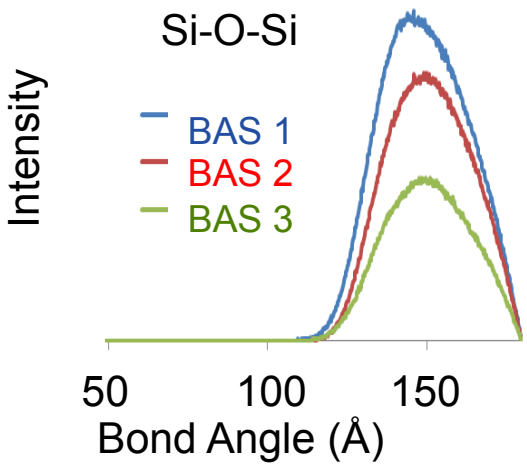
*A Pedone et al., "A new self-consistent empirical interatomic potential model for oxides, silicates, and silica-based glasses", J Phys Chem B, **110**, 11780-11795 (2006).

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

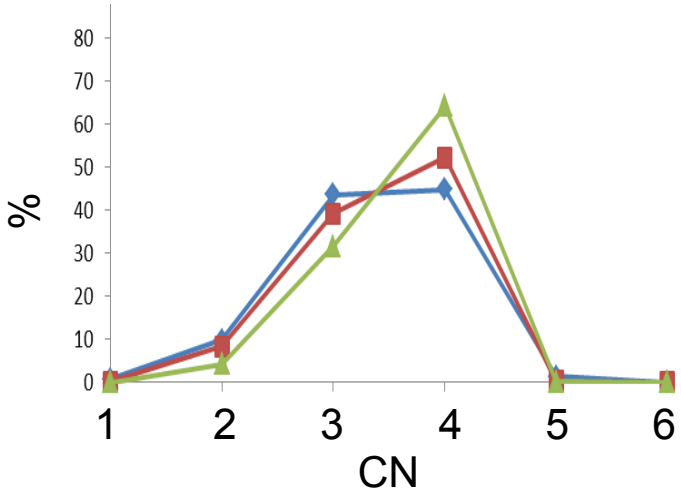
Structural Information (e.g., Non-Bridging Oxygens, NBOs) From MD & Theory Show Good Agreement

Glass	g/mole	Mole % Al_2O_3	NBO_{Th} (%)	NBO_{MD} (%)	$Connectivity_{Th}$ (BO/NF)
BAS 8	91.1	0	40.0	39.5	1.5
BAS 1	83.4	0	28.6	28.0	1.67
BAS 2	85.5	5	22.2	22.1	1.75
BAS 3	89.7	15	10.5	13.6	1.89

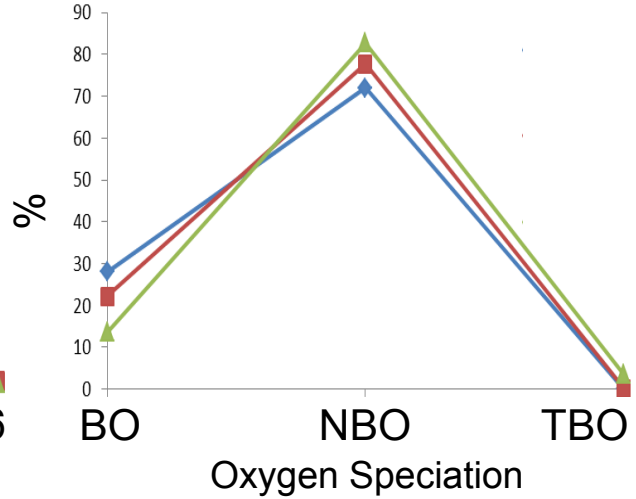
Peak position & symmetry increase from BAS 1→ 3



Q4/Q3 increases from BAS 1→3 (with decreasing NBOs)



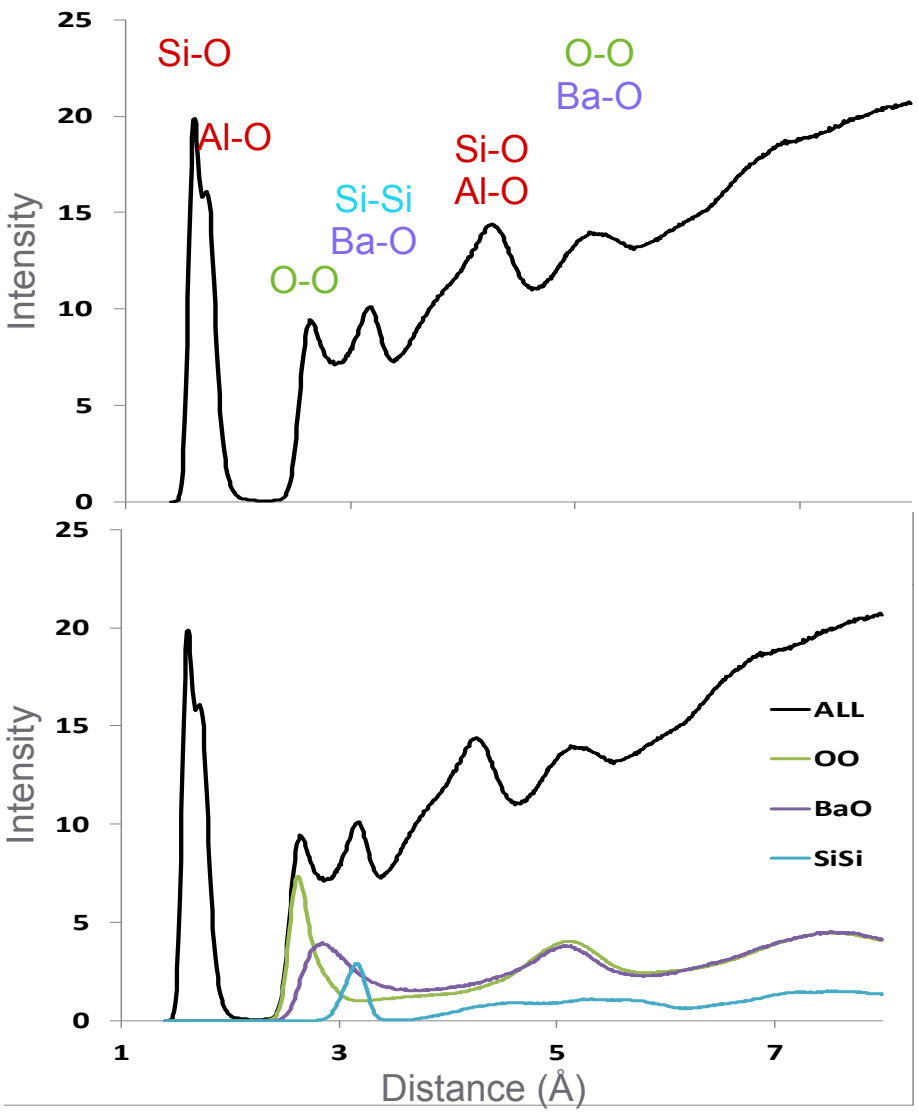
BOs:NBOs increases from BAS 1→3

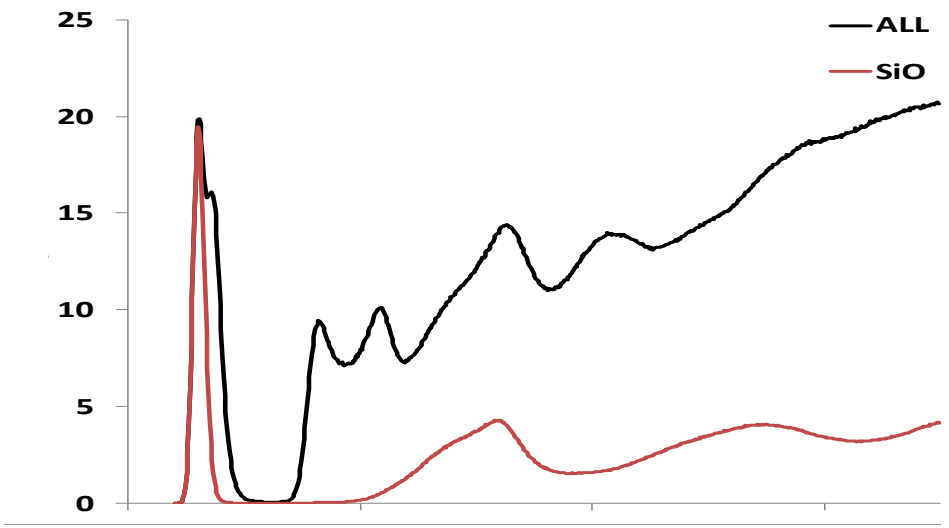


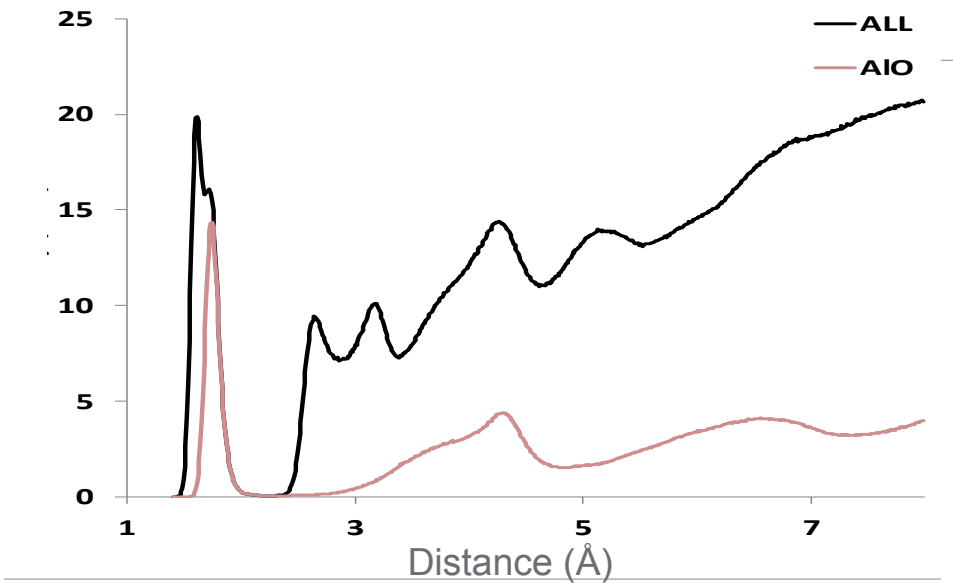
Comparisons to Experiment Have Been Used To Test & Validate Model Predictions

Tool	Bond Distances	Bond Assignments	Coordination Number	Non-Bridging Oxygens (NBOs)	Glasses
Model	Y	Y	Y	Bond Angle Distributions, BO's/ NBO's	BAS 1-3,8
aPDF	Y	inferred			BAS 1-3,8 BABS 5-7
NMR	Trends			Order/Disorder Trends	BAS 1-3,8 BABS 5-7
EXAFS	Y	Y (Ba)	Y (Ba)		BAS 1-3,8 BABS 5-7

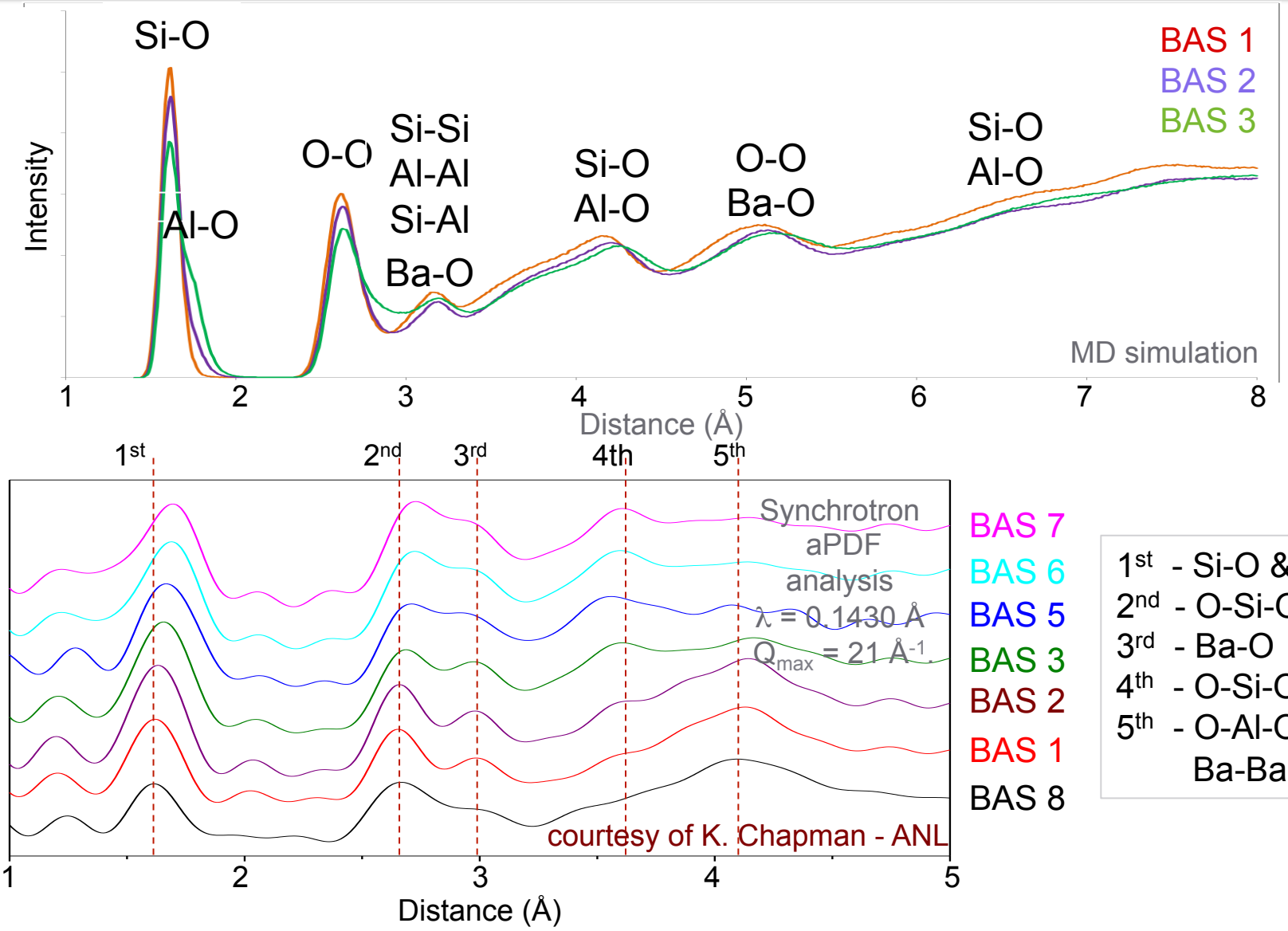
Molecular Dynamics Simulations Identify Specific Atom Separations With High Resolution





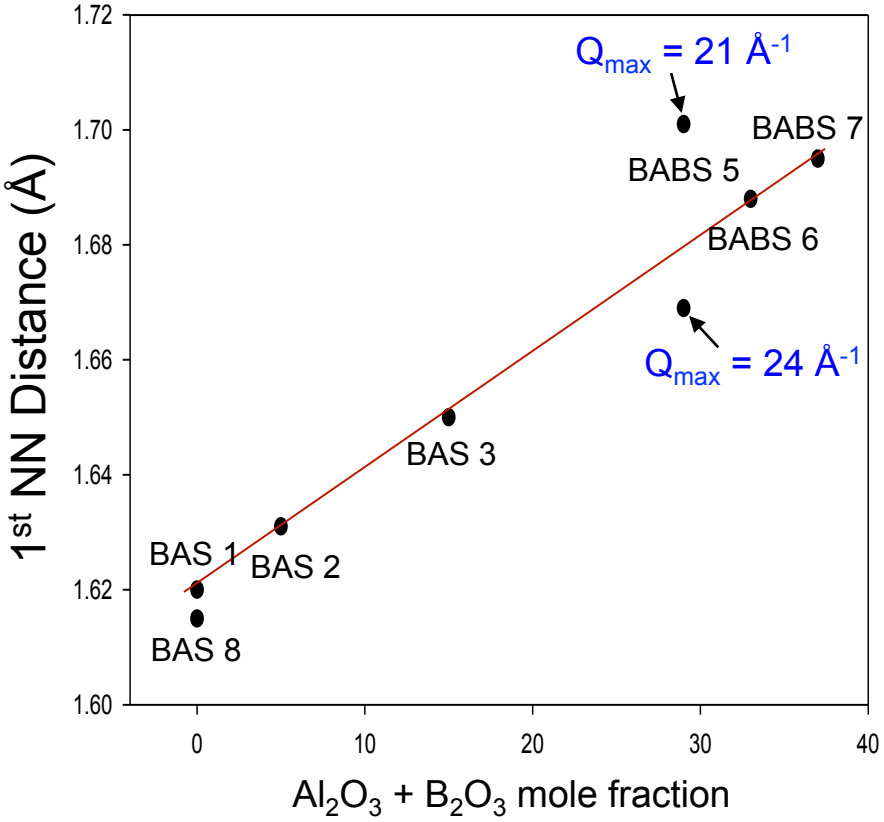


Assignments Of Measured aPDF Peaks Are Consistent With MD Simulations

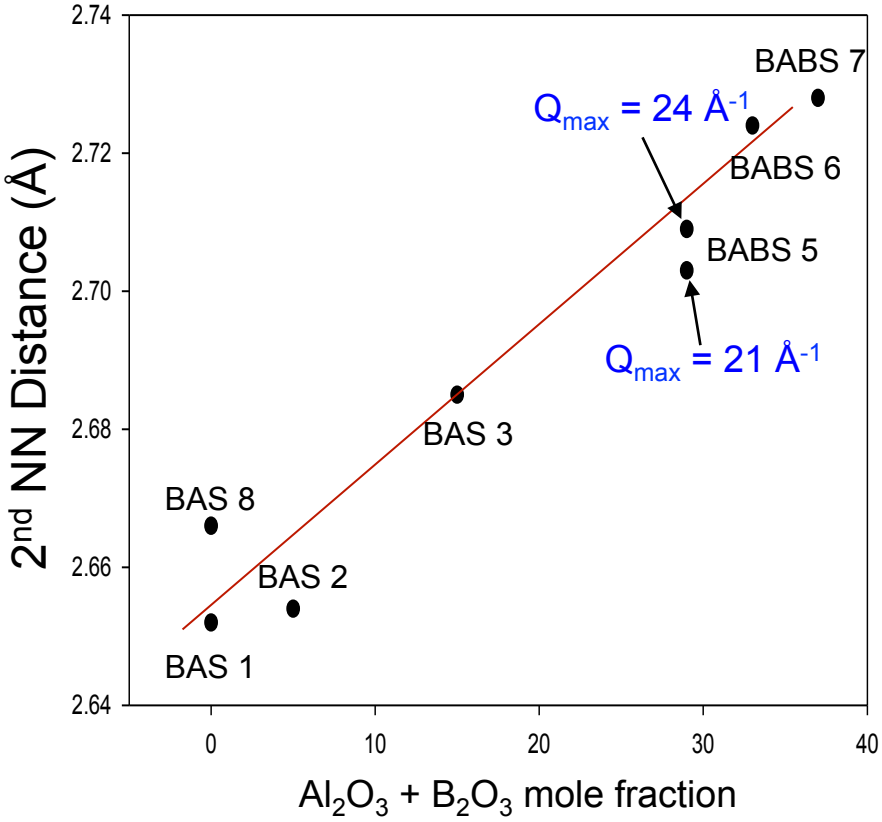


1st - Si-O & Al-O
2nd - O-Si-O
3rd - Ba-O
4th - O-Si-O-Si
5th - O-Al-O-Si-O
Ba-Ba

The 1st & 2nd Nearest Neighbor (NN) Separations In Glasses Are Related To The $Al_2O_3 + B_2O_3$ mole fraction

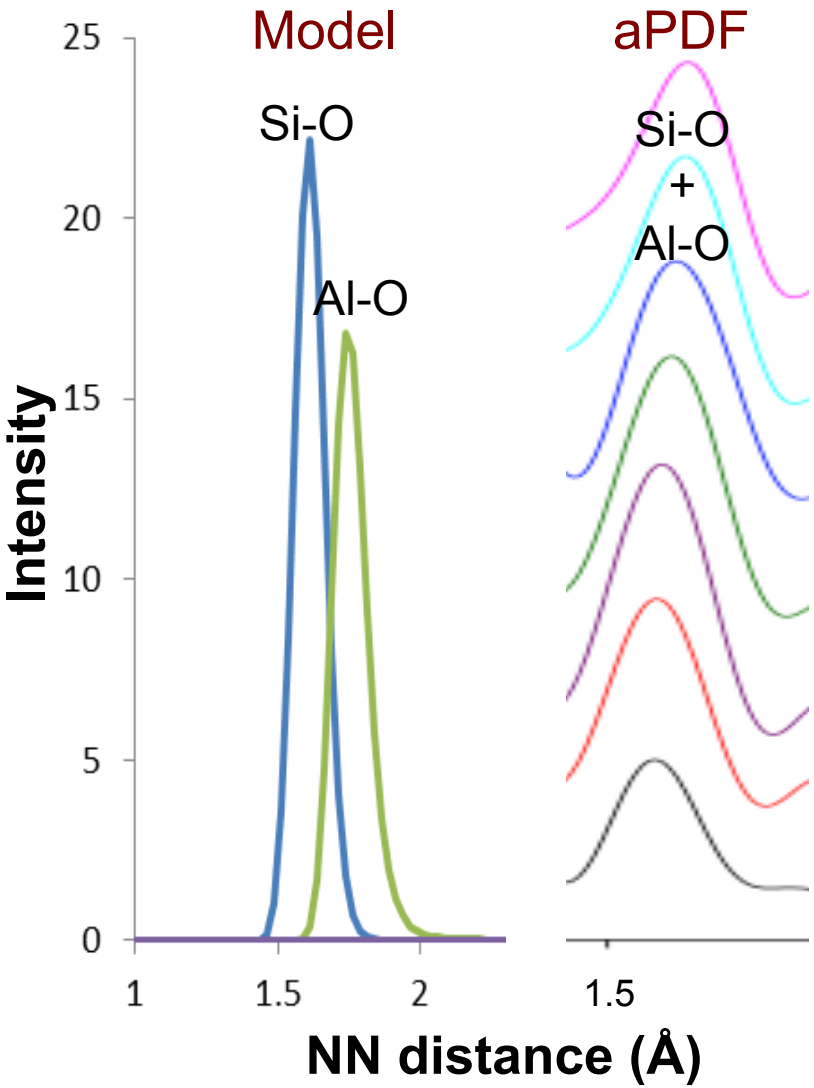


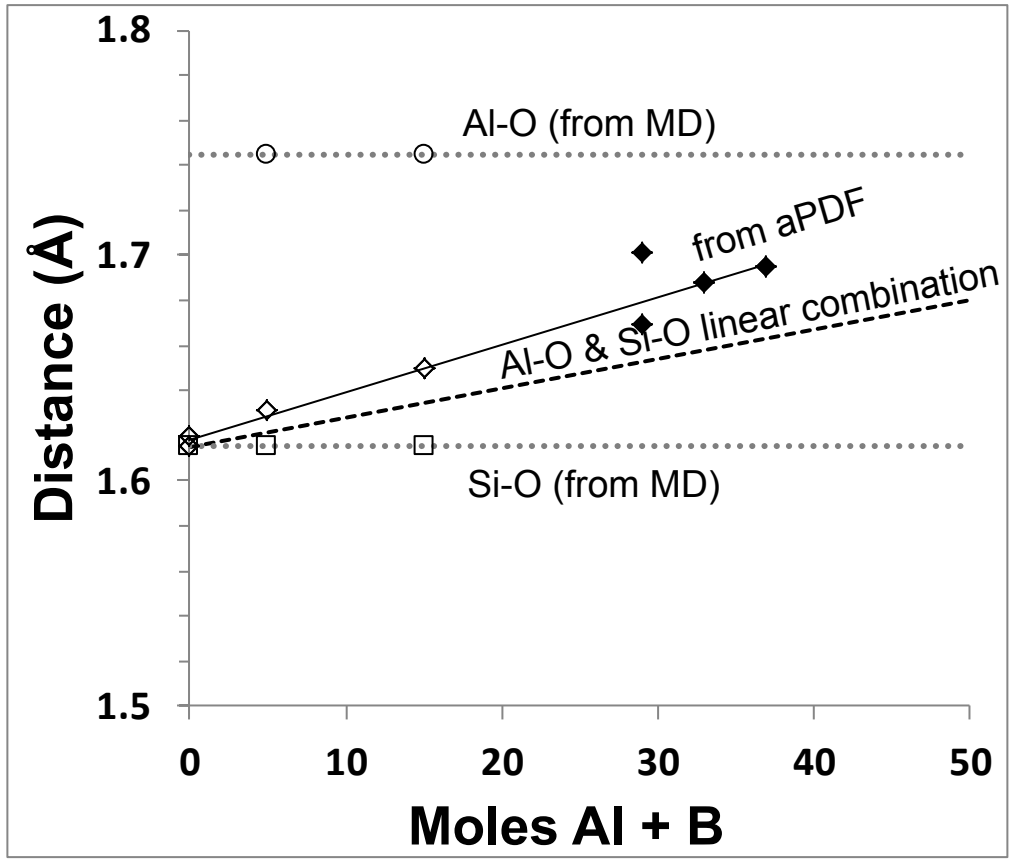
~0.002 Å increase in Si-O Bond length for every mole % addition of Al+B.



~0.002 Å increase in O-Si-O Bond length for every mole % addition of Al+B.

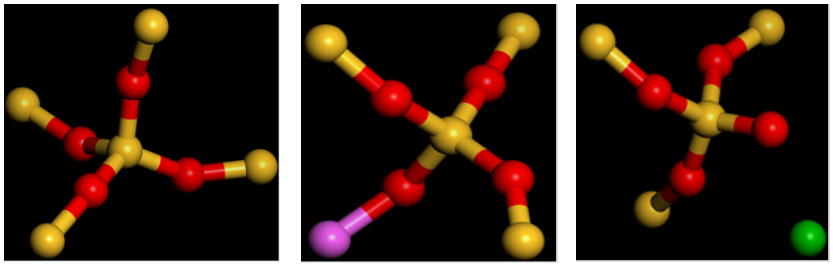
There Is A Minor Discrepancy Between The aPDF and MD 1st NN Peak Shifts





aPDF and NMR results show an increase in Al-O bond distance with increasing Al

^{29}Si MAS-NMR Q_3 & Q_4 Peaks Are Accurately Predicted From MD Coordinates, But The Q_3:Q_4 Ratios Differ

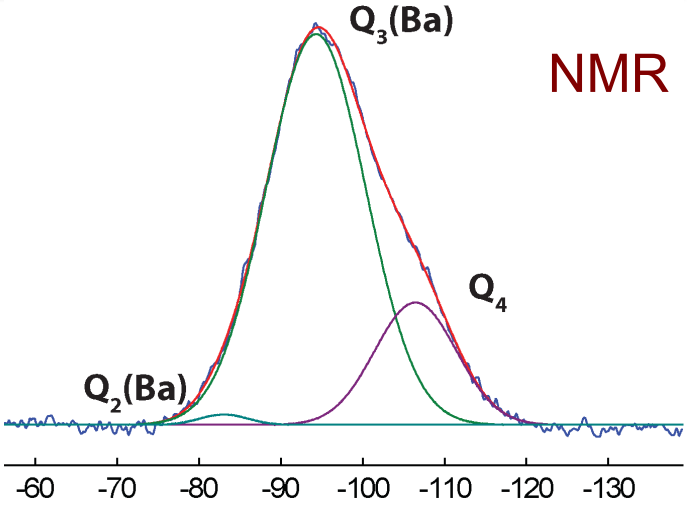


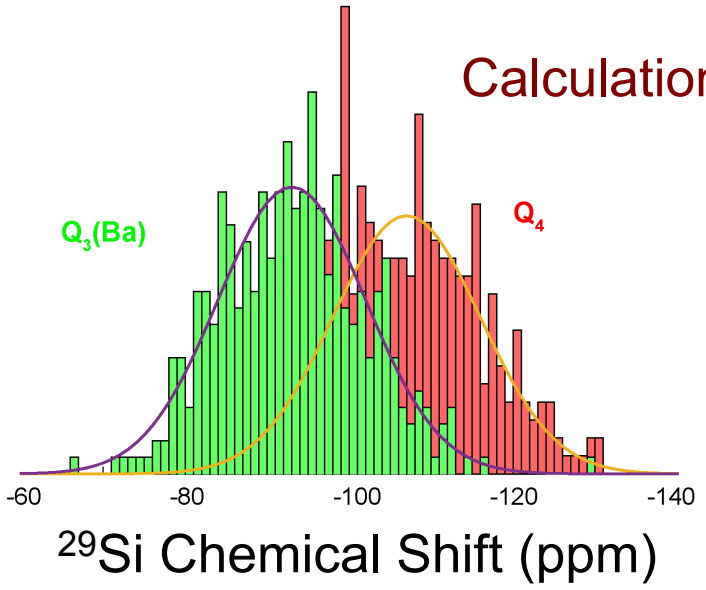
- Calculated ^{29}Si chemical shifts using MD coordinates.
- Employed correlation from Sherrif et al. (1991) based on silicate mineral structures.
- Factors included bond valence (s_i), angle of the bridging oxygen, Si-O bond distance, and distance to the 2nd nearest neighbors.

$$s_i = \left(\exp\left[\left(r_0 - r_i\right)/0.37\right]\right)$$

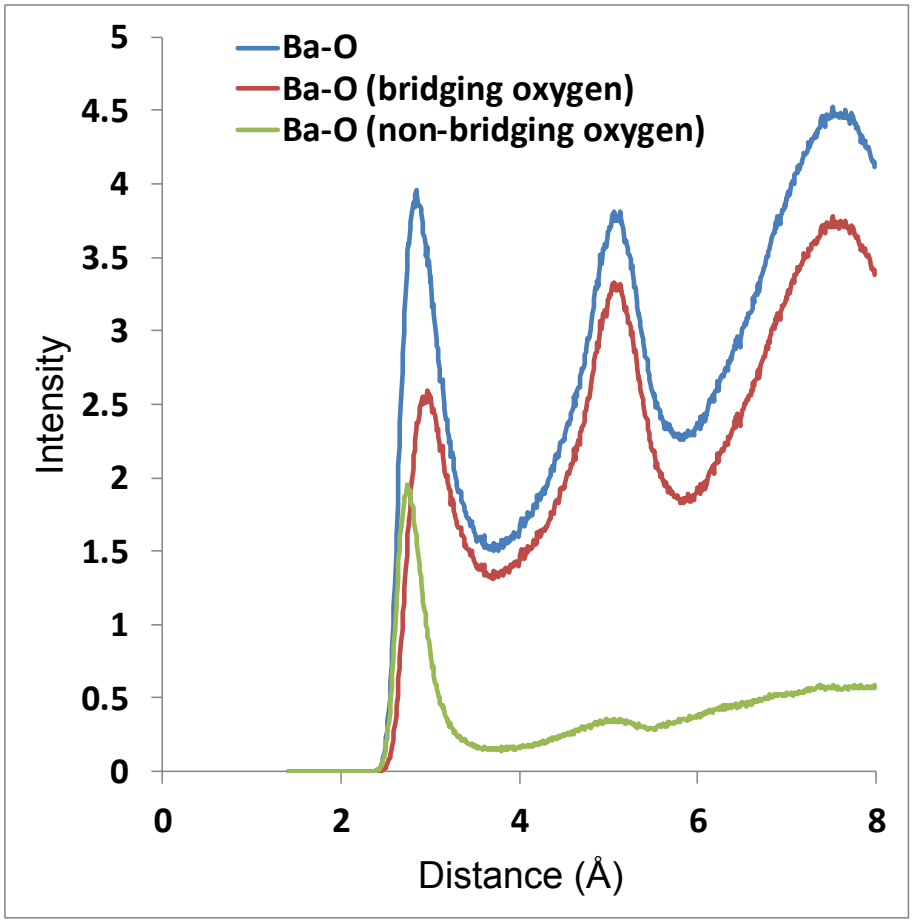
$$\Omega = \sum_{i=1}^{N}\left[s_i\left(1-3\cos^2\theta_i\right)/3R_i^3\right]\log D_i$$

$$\delta(^{29}\mathrm{Si}) = 701.6\Omega - 45.7$$

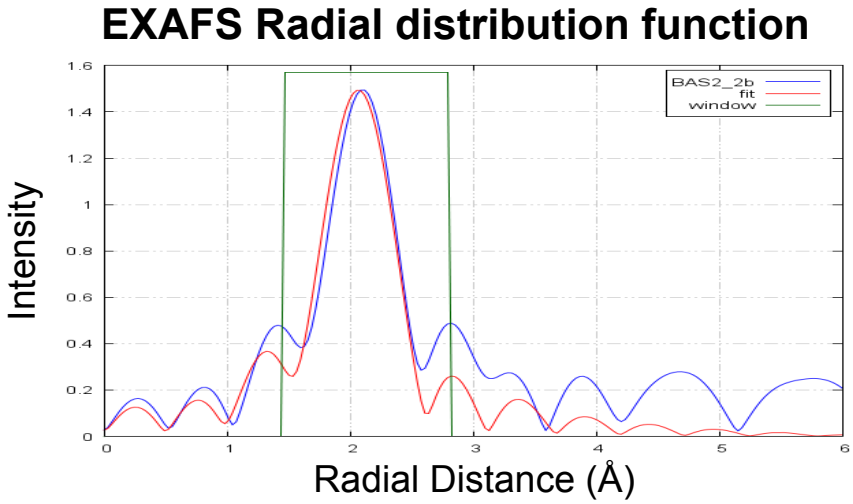


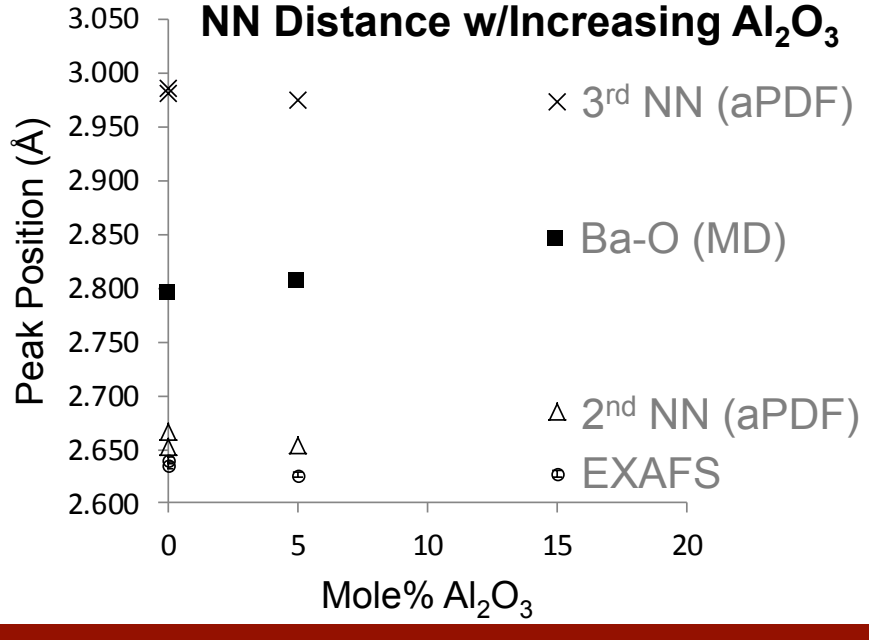


The Ba-O Distance From MD & Experiment Are Consistent With Mountjoy's Paper on Ba-S-O Glass



MD & experiment also indicate poorly-defined coordination numbers

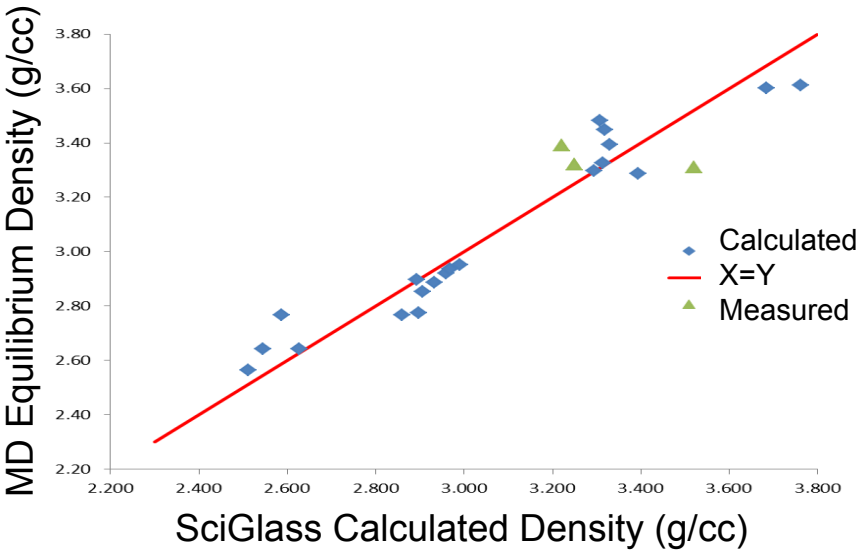


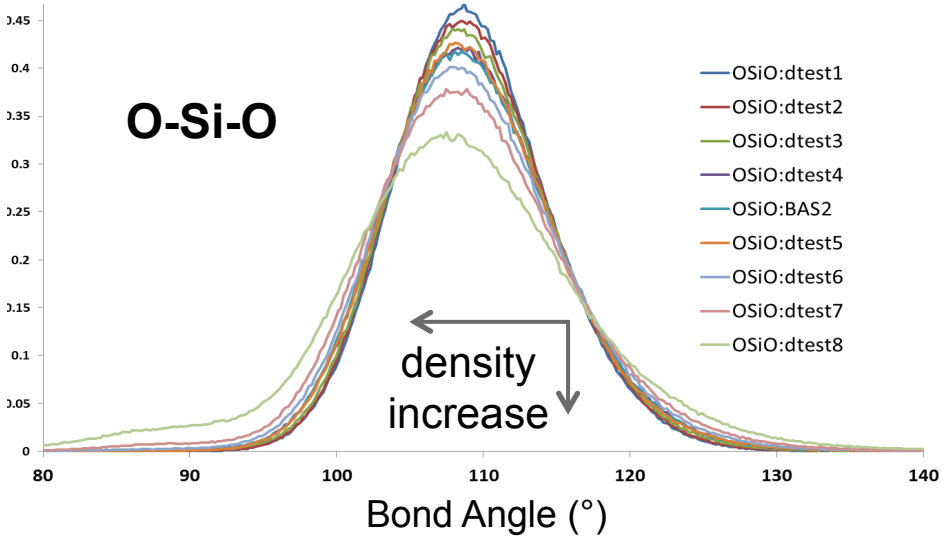


Input Density Affects Simulated Static Structure But Not Dynamic Equilibrium Structure

Glass	Archi-medes Density (g/cc)	He Pycnometer Density (g/cc)	SciGlass Density (g/cc)
BAS 8	3.60	3.69	3.69 ± 0.01
BAS 1	3.29	3.32	3.31 ± 0.01
BAS 2	3.31	3.31	3.32 ± 0.02
BAS 3	3.33	3.31	3.39 ± 0.01

Glass Name	density (g/cm^3)	Percent difference
BAS2	3.314	
dtest1	2.651	-20.00
dtest2	2.983	-10.00
dtest3	3.148	-5.00
dtest4	3.281	-1.00
dtest5	3.347	1.00
dtest6	3.480	5.00
dtest7	3.645	10.00
dtest8	3.977	20.00





Simulated & Measured BAS Glass Physical Properties Can Vary Considerably

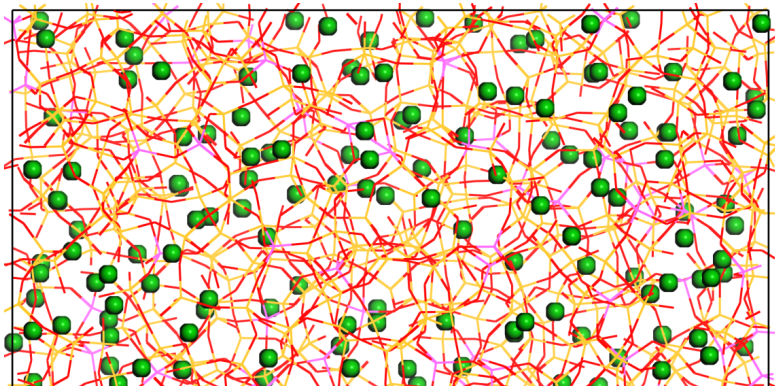
Glass	Measured T_g (°C)	Model T_g (°C)	Measured C_p (J/g K) @35 °C	Model C_p (J/g K)	*Calculated CTE (in/in/°C)	Model CTE Below Tg (in/in/°C)	Model CTE Above Tg (in/in/°C)
BAS 8	---	1532 ± 75	0.636	0.763 ± 0.006	8.31	14.4 ± 0.9	35.7 ± 2.4
BAS 1	---	1473 ± 95	---	0.858 ± 0.004	6.27	11.6 ± 0.5	31.0 ± 6.3
BAS 2	780	1365 ± 225	0.635	0.867 ± 0.004	6.52	10.4 ± 0.6	24.1 ± 6.1
BAS 3	751	1394 ± 116	0.619	0.884 ± 0.004	6.40	10.1 ± 0.4	19.1 ± 4.2
* At 300K using the Priven-2000 method inSciGlass							

MD Simulations show a decrease in CTE with increasing Al_2O_3, which is consistent with the higher connectivity structures with fewer NBOs created with the addition of Al_2O_3.

Simulated BAS And CAS Glasses Have Similar But Different Structures And Properties

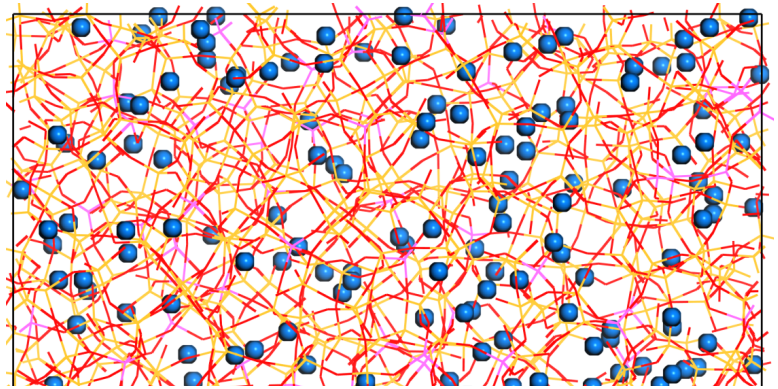
BAS 2

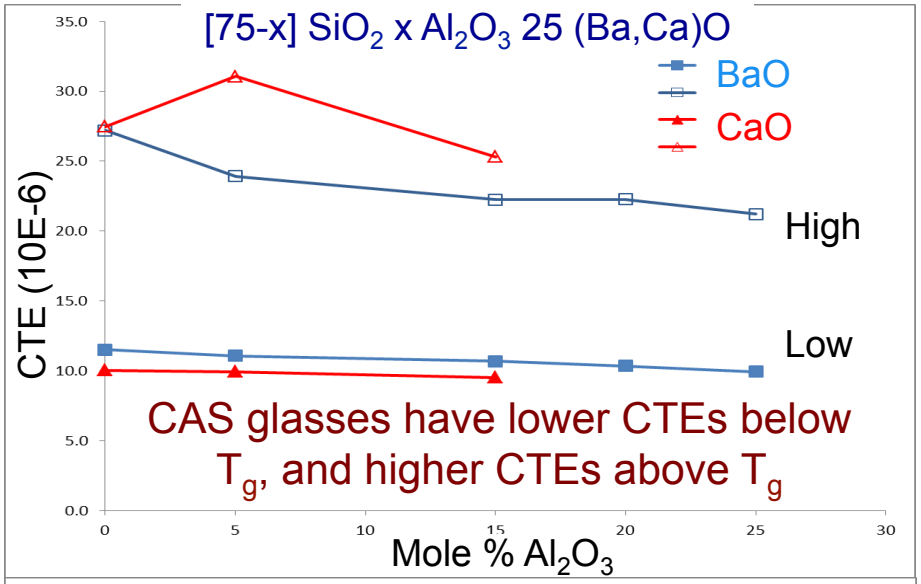
25 BaO - 5 Al_2O_3 - 70 SiO_2

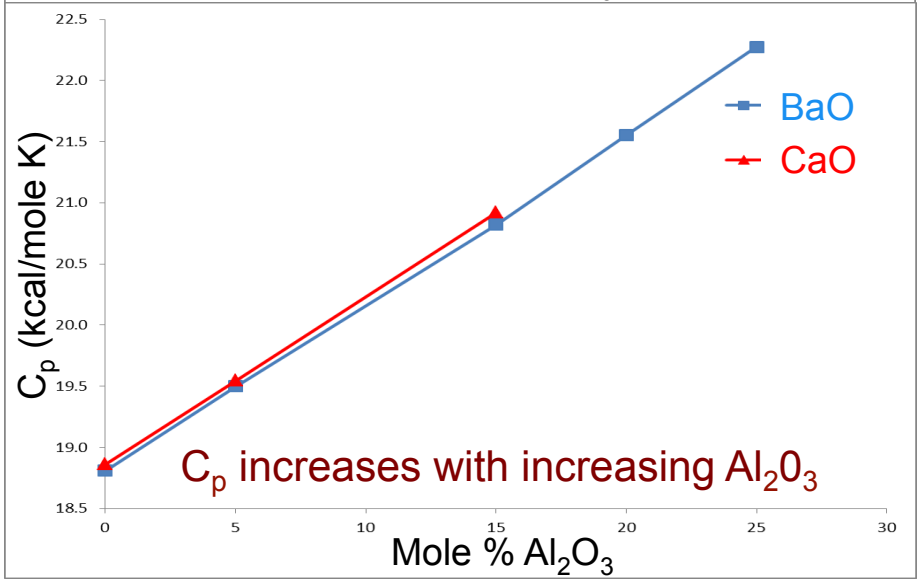


CAS 2

25 CaO - 15 Al_2O_3 - 60 SiO_2







More Complex Commercial BAS Sealing Glasses Were Simulated With Modifications

Original composition wt%

	SiO_2	Al_2O_3	BaO	CaO	B_2O_3	Na_2O	K_2O	PbO	Li_2O	MgO	SrO	CoO	Fe_2O_3	Sb_2O_3	ZrO_2	Cr_2O_3	Sr_2O_3	HfO_2	Total
T-1	66.82	3.51	12.02	0.11		7.24	7.21		0.62		0.02	0.13	0.07	0.6					98.35
S-1	68.8	3.59	11		0.0068	7.02	7.46		0.74	0.043		0.13	0.23	0.31		0.41			99.74
C-1	65.63	3.38	12.3	0.045	2.059	7.39	5.87		0.688	0.011			0.02		1.756	0.176	0.16	0.041	99.53
E-1	64.26	2.36	13.8	0.36	2.84	7.18	6.35	0.01	2.57	0.14	0.13								100.00

Drop components < mol 1%

	SiO_2	Al_2O_3	BaO	CaO	B_2O_3	Na_2O	K_2O	PbO	Li_2O	MgO	SrO	CoO	Fe_2O_3	Sb_2O_3	ZrO_2	Cr_2O_3	Sr_2O_3	HfO_2	Total
T-1	66.82	3.51	12.02			7.24	7.21		0.62										97.42
S-1	68.8	3.59	11			7.02	7.46		0.74										98.61
C-1	65.63	3.38	12.3			7.39	5.87		0.688						1.756				97.01
E-1	64.26	2.36	13.8			7.18	6.35		2.57										96.52

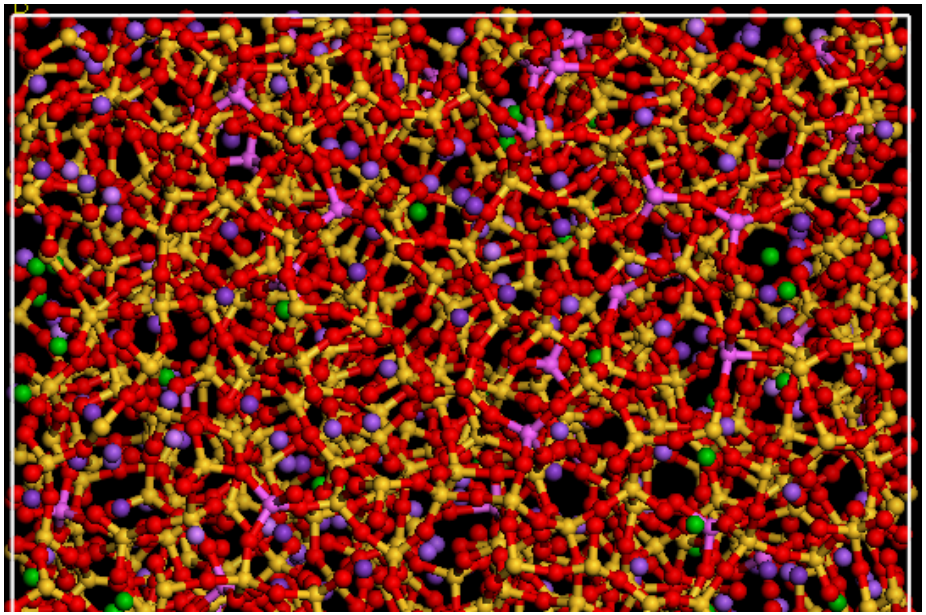
Normalized wt%

	SiO_2	Al_2O_3	BaO	CaO	B_2O_3	Na_2O	K_2O	PbO	Li_2O	MgO	SrO	CoO	Fe_2O_3	Sb_2O_3	ZrO_2	Cr_2O_3	Sr_2O_3	HfO_2	Total
T-1	68.6	3.6	12.4			7.4	7.5		0.6										100.00
S-1	69.8	3.6	11.2			7.1	7.5		0.8										100.00
C-1	67.6	3.5	12.7			7.6	6.0		0.7						1.8				100.00
E-1	66.6	2.5	14.3			7.5	6.6		2.7										100.00

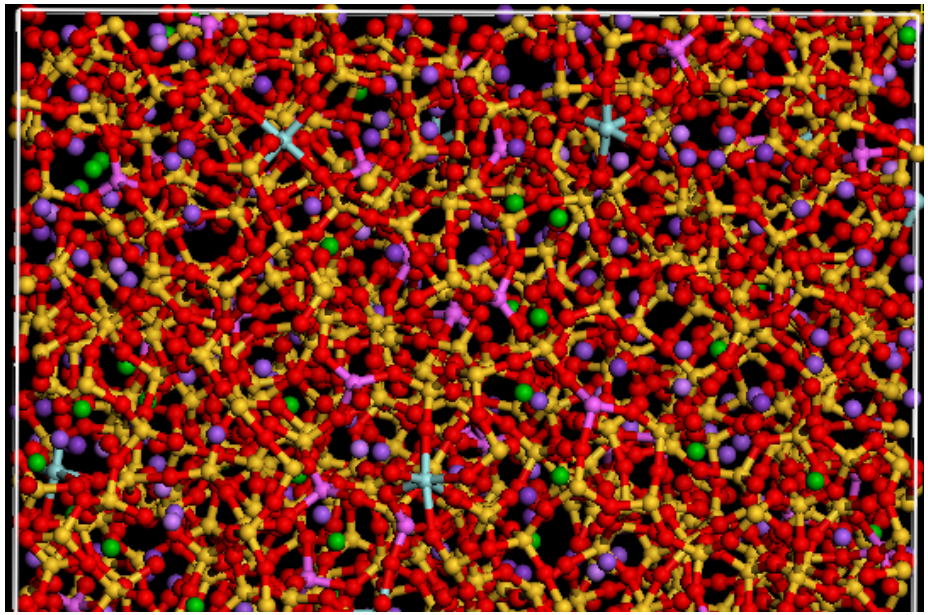
Atoms in simulation

	SiO_2	Al_2O_3	BaO	CaO	B_2O_3	Na_2O	K_2O	PbO	Li_2O	MgO	SrO	CoO	Fe_2O_3	Sb_2O_3	ZrO_2	Cr_2O_3	Sr_2O_3	HfO_2		Total
	Si	Al	Ba	Ca	B	Na	K	Pb	Li	Mg	Sr	Co	Fe	Sb	Zr	Cr	Sr	Hf	O	
T-1	850	52	60			178	118		32										2002	3292
S-1	857	52	54			170	118		38										2009	3298
C-1	843	52	62			184	96		36						11				2006	3290
E-1	810	36	68			176	102		130										1946	3268

Simulated "Equivalent" Commercial Glasses With 6-7 Components Have Similar Structures And Properties



T-1



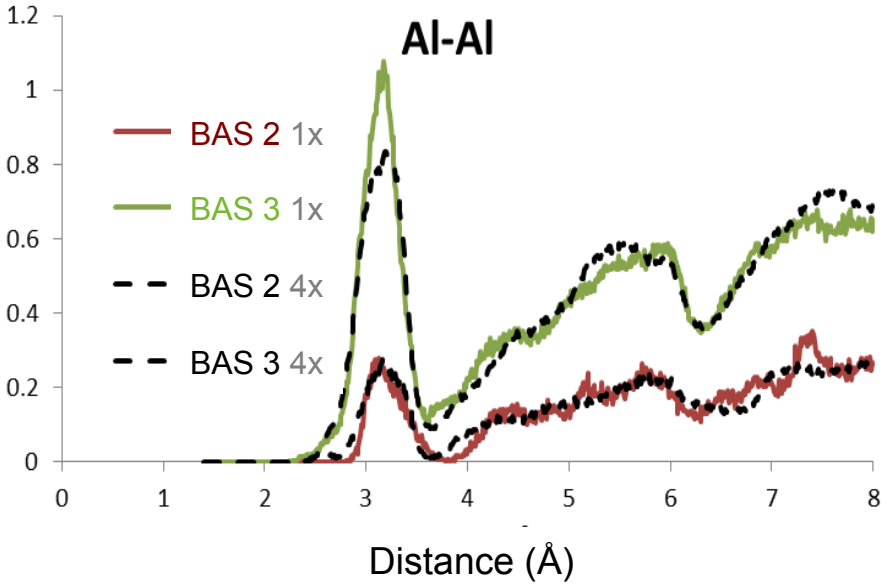
C-1

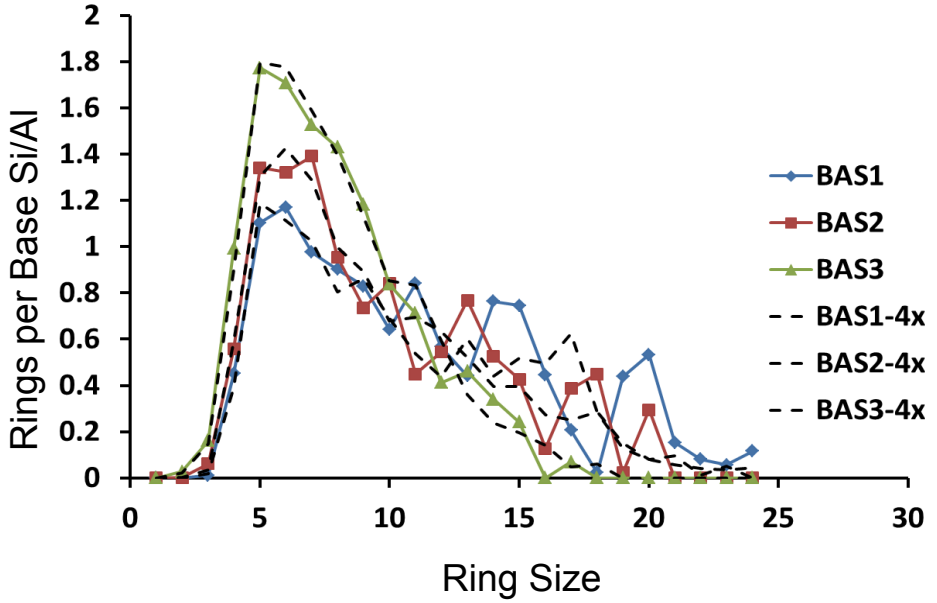
Glass	Density (g/cc)	Model T_g (°C)	Model C_p (J/g K)	CTE Below Tg (in/in/°C)	CTE Above Tg (in/in/°C)
S-1	2.58	1618 ± 111	1.176 ± 0.010	14.9 ± 0.8	30.2 ± 7.8
T-1	2.59	1453 ± 157	1.166 ± 0.007	13.8 ± 0.3	22.3 ± 3.9
C-1	2.64	1647 ± 147	1.154 ± 0.000	13.0 ± 1.2	27.9 ± 5.8

Modeling Results Can Be Affected By The Number Of Atoms In The Simulation

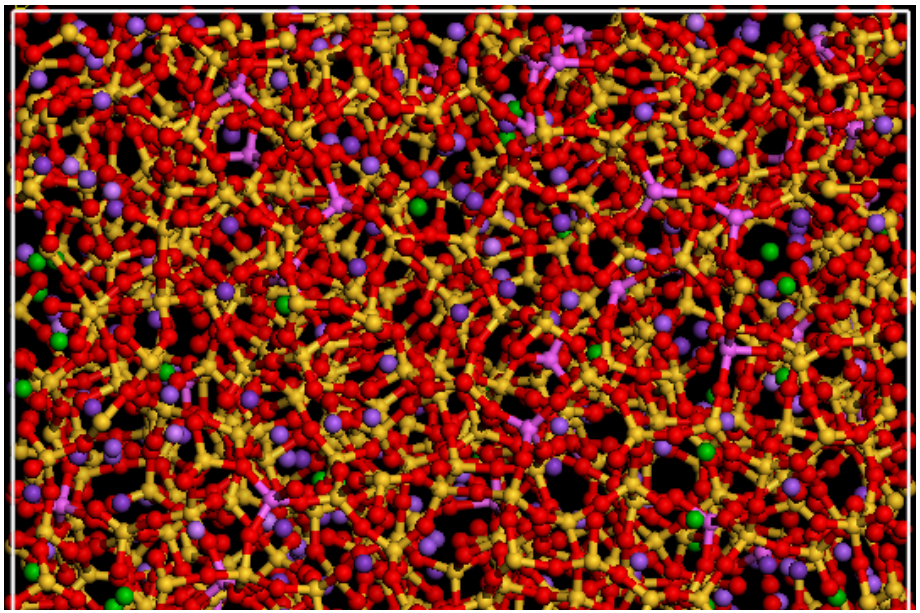
25 BaO – X Al_2O_3 – (75-x) SiO_2 Glasses

Glass	Oxide Mole %			Initial 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	3.31	275/1100	0/0	825/3300	1925/7700	3025/12100	35.108/55.731
BAS 2	25	5	70	3.32	275/1100	110/440	770/3380	1980/7200	3125/12540	36.354/57.709
BAS 3	25	15	60	3.39	275/1100	330/1320	660/2640	2090/8360	3355/13420	37.053/58.818

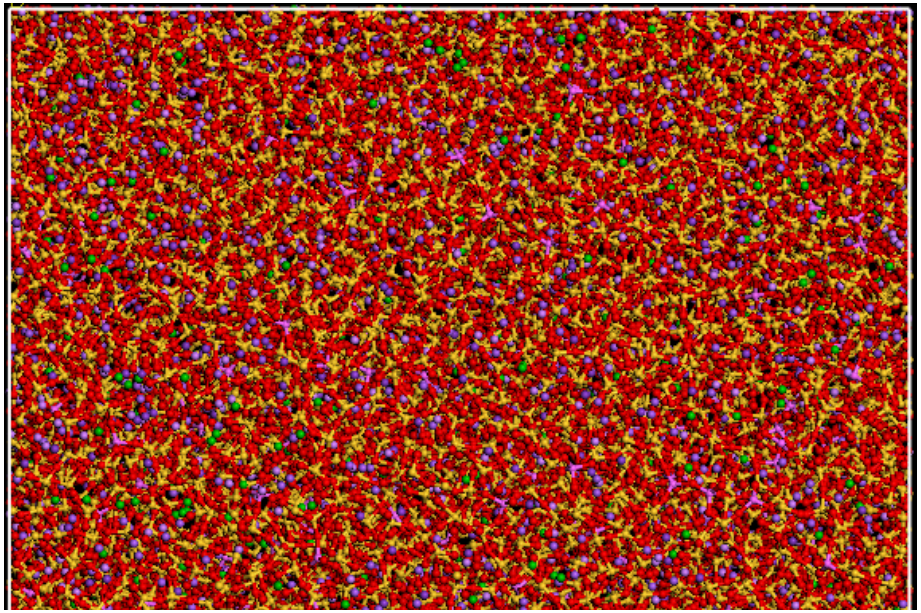




Much Larger Simulations And Longer Times Are Required To Model Elements At < 1 Mole %



T-1 – 3,293 atoms

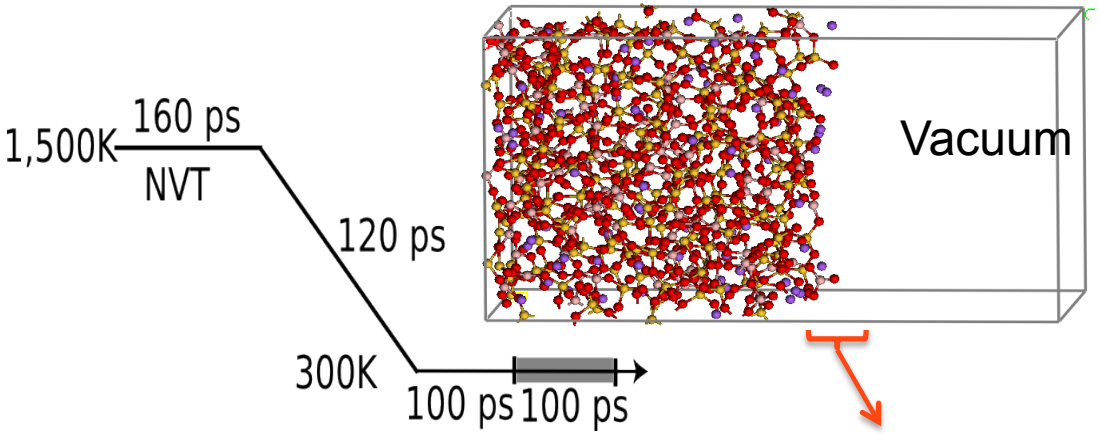


T-1 – 32,927 atoms

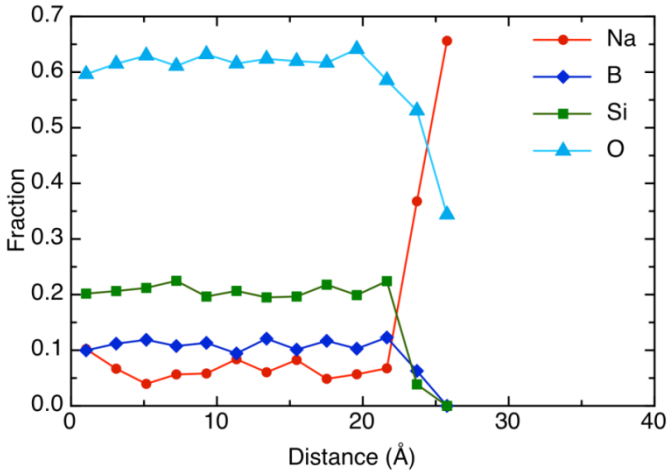
- Interface modeling has commenced - a more practical approach for minor active elements?

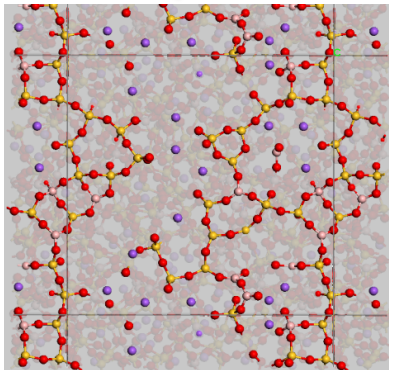
The Migration Of Surface Active Elements To An Interface May Enable Improved MD Simulations

MD simulations of Na-borosilicate glass surfaces



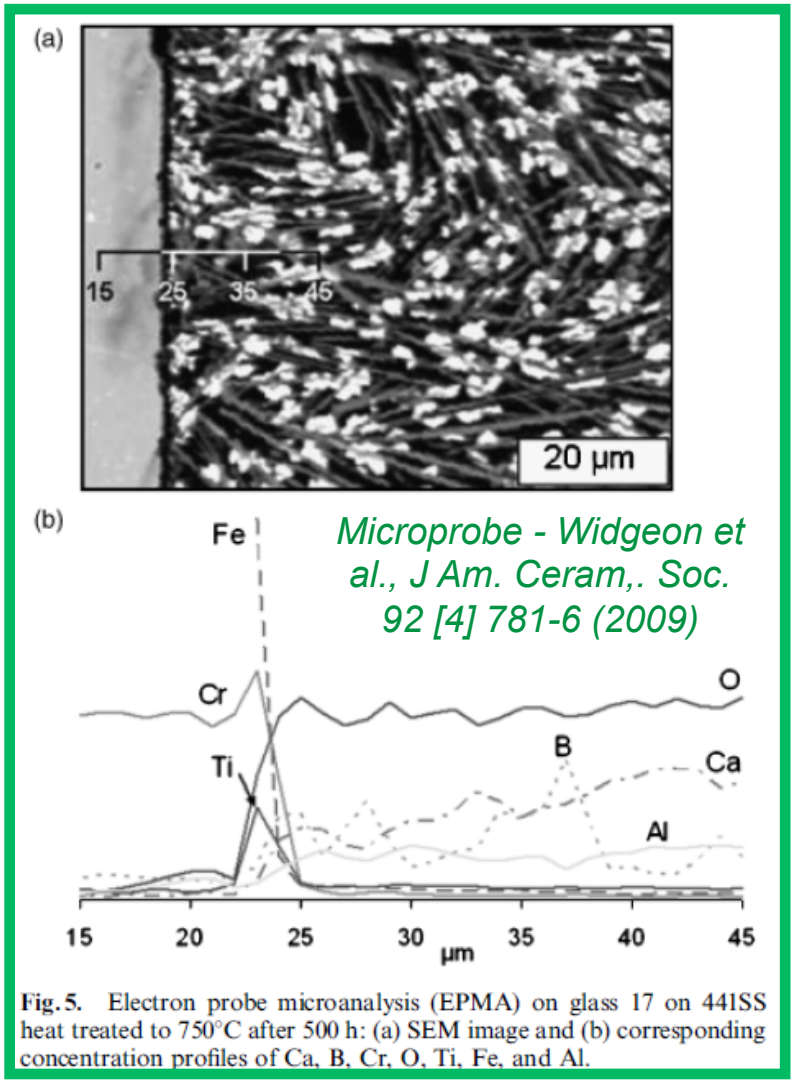
Fraction of atoms vs. distance





Top 4 Å

Composition-dependent FF (Kieu et al. 2011)



Microprobe - Widgeon et al., J Am. Ceram,. Soc. 92 [4] 781-6 (2009)

Fig. 5. Electron probe microanalysis (EPMA) on glass 17 on 441SS heat treated to 750°C after 500 h: (a) SEM image and (b) corresponding concentration profiles of Ca, B, Cr, O, Ti, Fe, and Al.

Experimentally-Validated Glass Structure And Property Models Are Being Developed To Enable FGC Design

- **Summary**
  - Melted & Characterized BaO-Al_2O_3-SiO_2 (BAS) & BaO-Al_2O_3-B_2O_3-SiO_2 (BABS) glasses
    - Characterized glass chemistry (XPS), structure (XAFS, NMR, & aPDF) & physical properties
  - Simulated 3 component model glasses, and 6-7 component commercial glasses
    - Applied Pedone interatomic potentials in LAMMPS MD code
    - Completed sensitivity analysis
      - Modeling minor constituent is challenging
      - Dynamic simulations insensitive to input density
    - Adapted/applied post-processing tools to analyze glass structure & properties
  - Compared/contrasted results from modeling & experiment
    - Good first-order agreement for structure
      - Some room to improve potentials
    - Variable results for properties
      - Good agreement for density
      - Predicting physical properties is challenging
- **Future Work**
  - Refine experiments/analyses
    - Higher resolution experiments
  - Advance glass modeling
    - Extend modeling to glass interfaces.
    - Develop/apply capability to model B