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Modeling and Characterization of Glasses for Hermetic Sealing Applications

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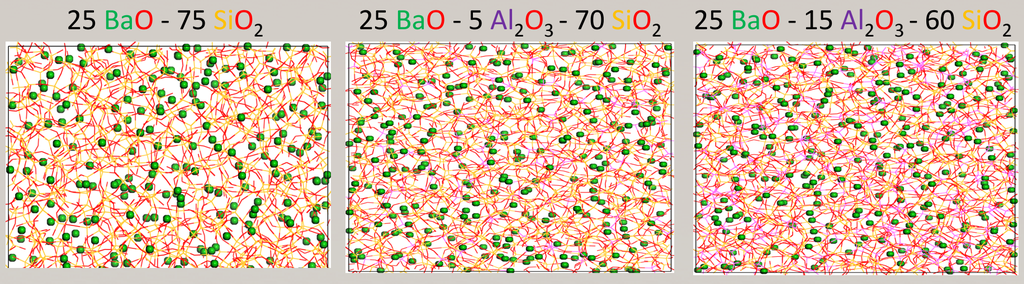
Objective: Develop experimentally-validated modeling/simulation tools to predict/control glass chemistry-structure-property relations

Barium Alumino-Silicate (BAS) Glasses Were Simulated With The LAMMPS** Molecular Dynamics (MD) Code & Pedone* Multicomponent Force Field

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

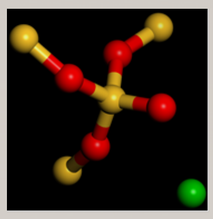


Glass	Oxide Mole % BaO	Al_2O_3	SiO_2	Archimedes Density (g/cc)	Number of Atoms (in 1x/4x Simulation) Ba	Al	Si	O	Total	Box Length (Å)
BAS 1	25		75	3.52	275/ 1100	0/ 0	825/ 3300	1925/ 7700	3025/ 12100	35.108/ 55.731
BAS 2	25	5	70	3.25	275/ 1100	110/ 440	770/ 3380	1980/ 720	3125/ 12540	36.354/ 57.709
BAS 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).

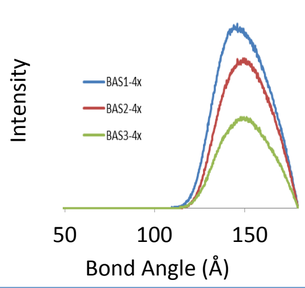
S Plimpton, "Fast Parallel Algorithms for Short-Range Molecular-Dynamics, J Comp Phys, **117 [1], 1-19 (1995).

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

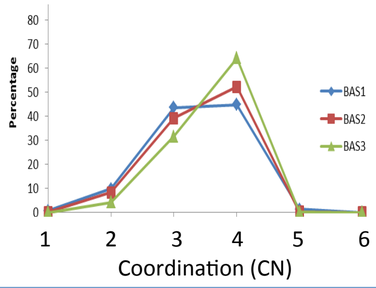


Glass	g/mole	Mole % Al_2O_3	NBO_{Th} (%)	NBO_{MD} (%)	$Connectivity_{Th}$ (BO/NF)
BAS 8	91.1	0	40.0	39.5	1.5
BAS 1	83.4	0	28.6	28.0	1.67
BAS 2	85.5	5	22.2	22.1	1.75
BAS 3	89.7	15	10.5	13.6	1.89

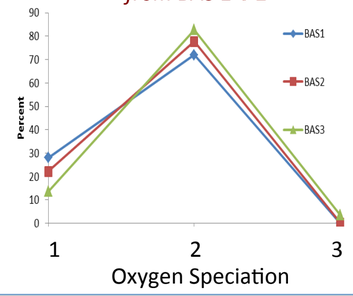
Peak position & symmetry increase from BAS 1→ 3



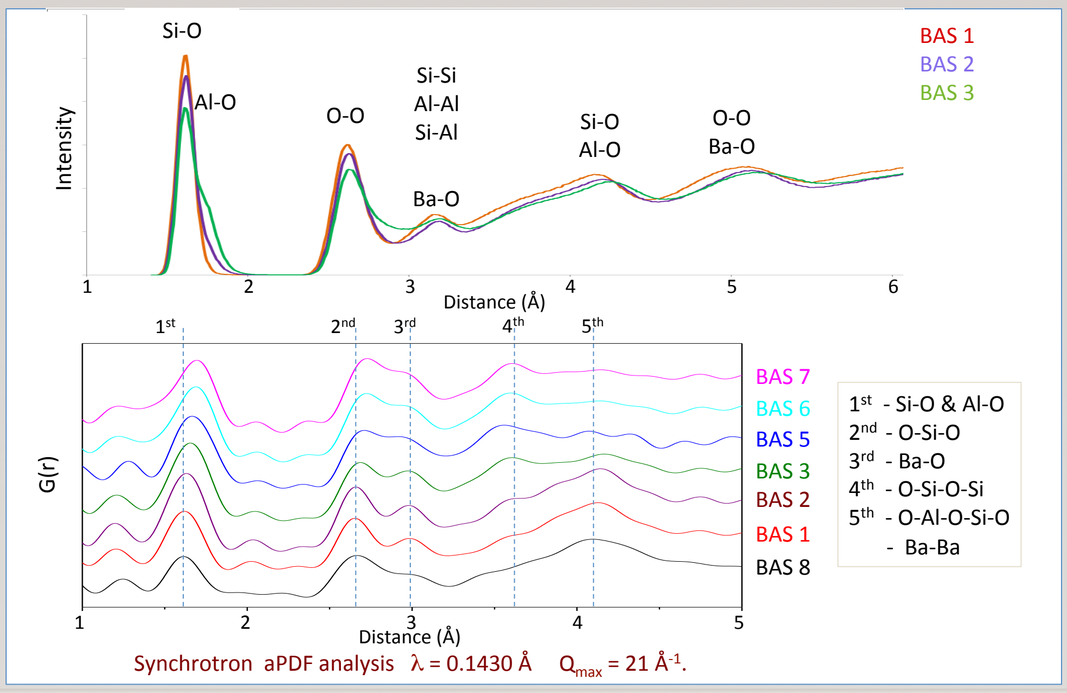
Q4/Q3 increases from BAS 1→3 (with decreasing NBOs)



BOs:NBOs increases from BAS 1→2

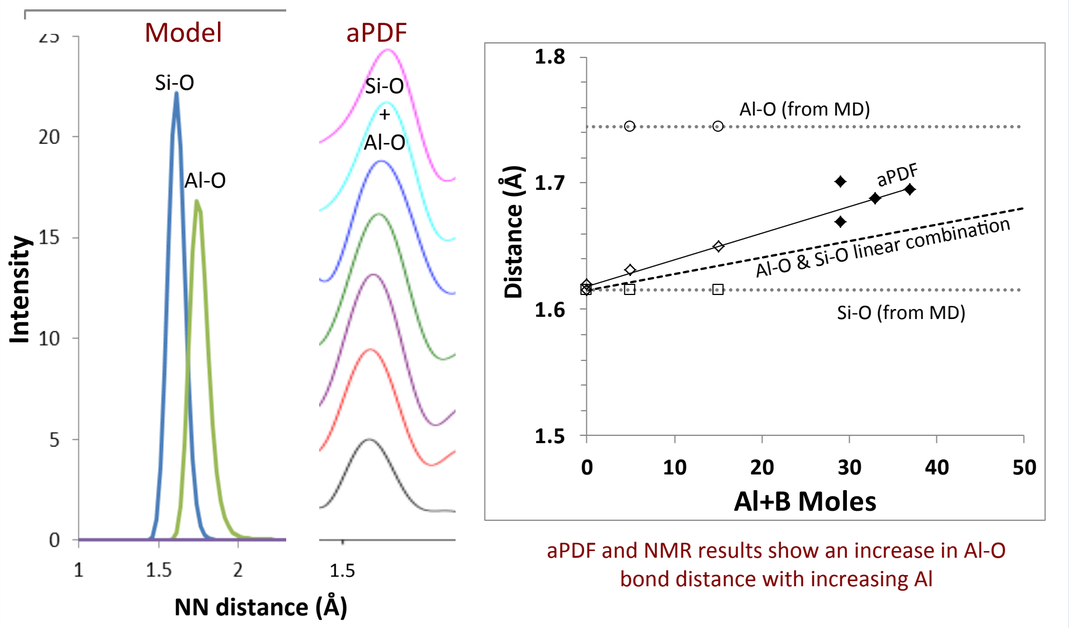


Nearest Neighbor (NN) Distances From Atomic Pair Distribution Function (aPDF) Analysis Are Consistent With MD Simulation



Synchrotron aPDF analysis $\lambda = 0.1430$ Å $Q_{max} = 21$ Å^{-1}.

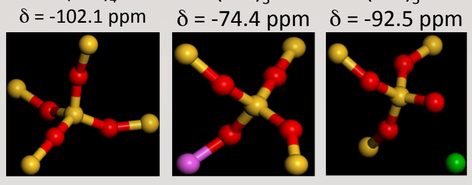
There Is A Discrepancy Between The aPDF and MD 1st NN Peak Shifts



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 Ratio Differs

$Si(OSi)_4$ δ = -102.1 ppm | $Si(OSi)_3Al$ δ = -74.4 ppm | $Si(OSi)_3Ba$ δ = -92.5 ppm

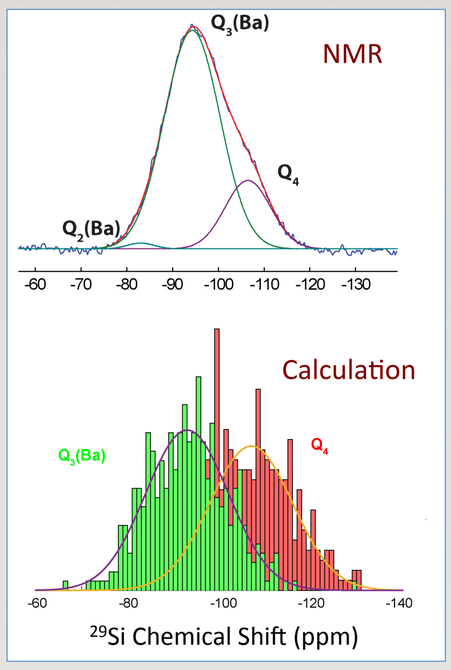


- Calculated ^{29}Si chemical shifts using MD coordinates.
- Employed correlation from Sherrif et al. (1991) based on silicate mineral structures.
- Factors included bond valence (s_i), angle of the bridging oxygen, Si-O bond distance, and distance to the 2nd nearest neighbors.

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

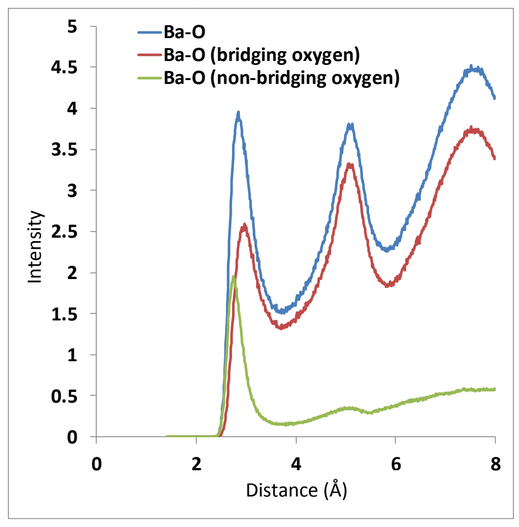
$$\Omega = \sum_{i=1}^{N}\left[s_i\left(1-3\cos^2\theta_i\right)/3R_i^3\right]\log D_i$$

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

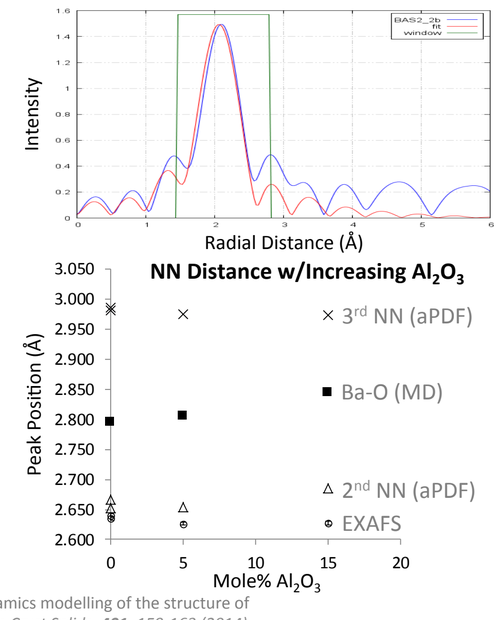


Ba-O Distances From Experiment Are Consistent With Raj and Mountjoy, But Differ From MD Simulations With The Original Ba Potential

MD pair distribution function



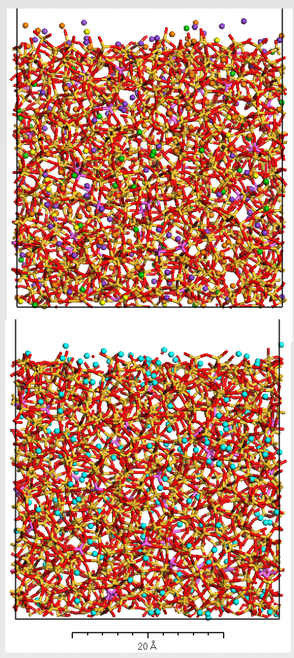
EXAFS Radial distribution function

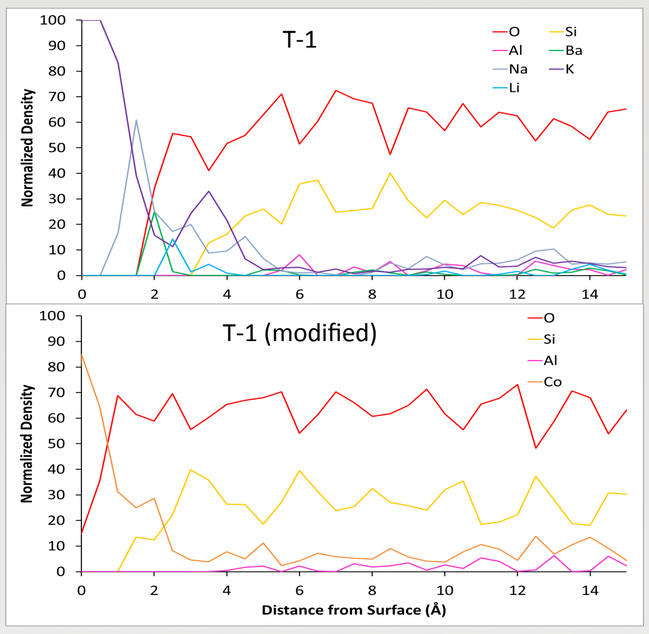


- Ba creates NBOs
- MD & experiment indicate poorly-defined CNs

M Raj & G Mountjoy, "Molecular dynamics modelling of the structure of barium silicate glasses $BaO–SiO_2$, *J Non Cryst Solids*, ***401***, 159-163 (2014).

MD Simulations Show That Glass Network Modifiers In A Commercial Sealing Glass Migrate To The Surface Of The Glass





Simulated & Measured BAS Glass Physical Properties Can Vary Considerably

Structure-Property relationships informed from modeling and experiment

Glass	Exp. T_g (°C)	MD T_g (°C)	Exp. C_p (J/g K) @35 °C	MD C_p (J/g K)	Exp. CTE (in/in/°C)	*Calc. CTE (in/in/°C)	MD CTE Below Tg (in/in/°C)	Model CTE Above Tg (in/in/°C)
BAS 8	695	1532 ± 75	0.636	0.763 ± 0.006	9.74	8.31	14.4 ± 0.9	35.7 ± 2.4
BAS 1	706	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	7.34	6.52	10.4 ± 0.6	24.1 ± 6.1
BAS 3	751	1394 ± 116	0.619	0.884 ± 0.004	6.68	6.40	10.1 ± 0.4	19.1 ± 4.2
* At 300K using the Priven-2000 method in SciGlass								

MD Simulations show a decrease in CTE with increasing Al_2O_3, which is consistent with the increased network connectivity (e.g., fewer NBOs) with increasing Al_2O_3 content.

X-ray fluorescence (XRF) chemical analysis of some commercial sealing glasses

	#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				

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