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

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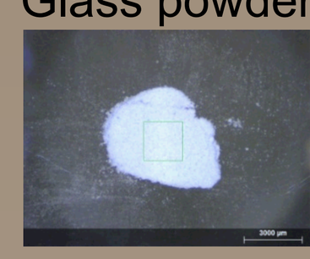
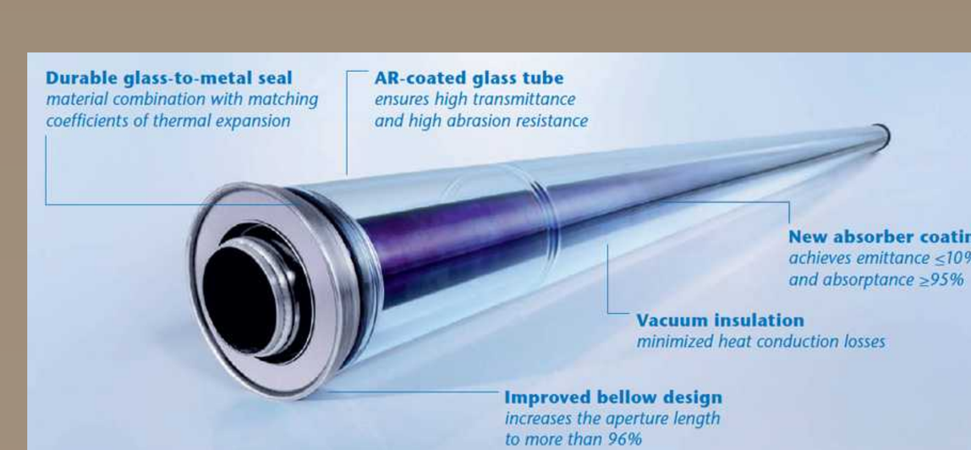
Summary. *The performance of joining materials in many applications, such as glass-to-metal seals in solid oxide fuel cells and medical devices, require improvements in glass properties for greater reliability. In this work, simple sealing glass compositions have been used to develop experimentally-validated molecular models. The goal is to understand glass chemistry and structure such that modeling can be used to optimize glass design, manufacturability, and performance. The coupled modeling and experimental work are discussed.*

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

Glass powder





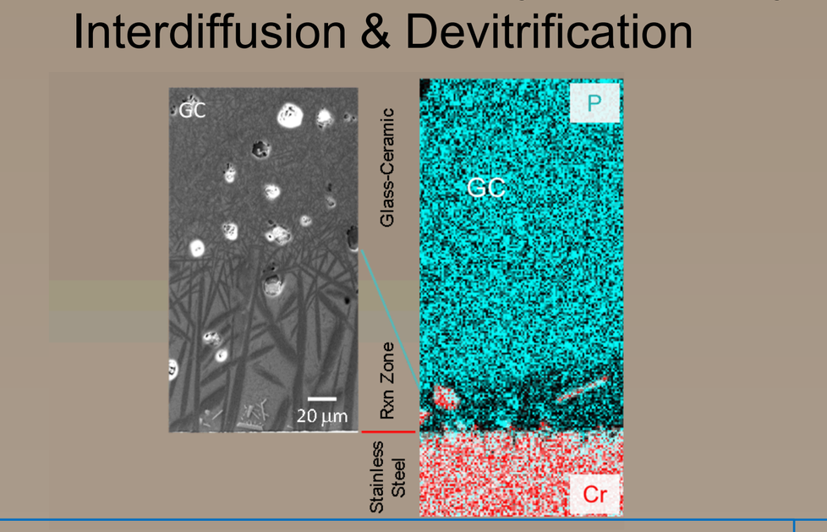
http://www.us.schott.com/csp/english/schott-solar-ptr-70-receivers.html

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)

Sealing materials suffer from processing and performance complexities

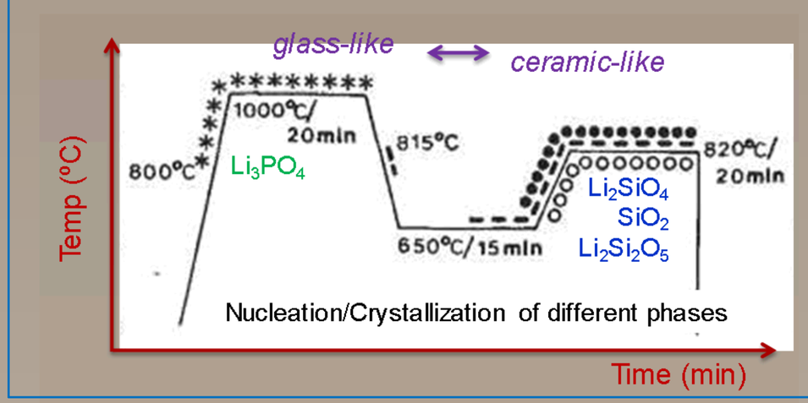
Glass for Glass-to-Metal (GtM) Sealing
+ Processability
+ Materials Compatibility
+ Durability
- Low CTE
- Low toughness/crack tolerance
- Reactivity & Stability

Seal/Interface Is Adversely Affected By Interdiffusion & Devitrification



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

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

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

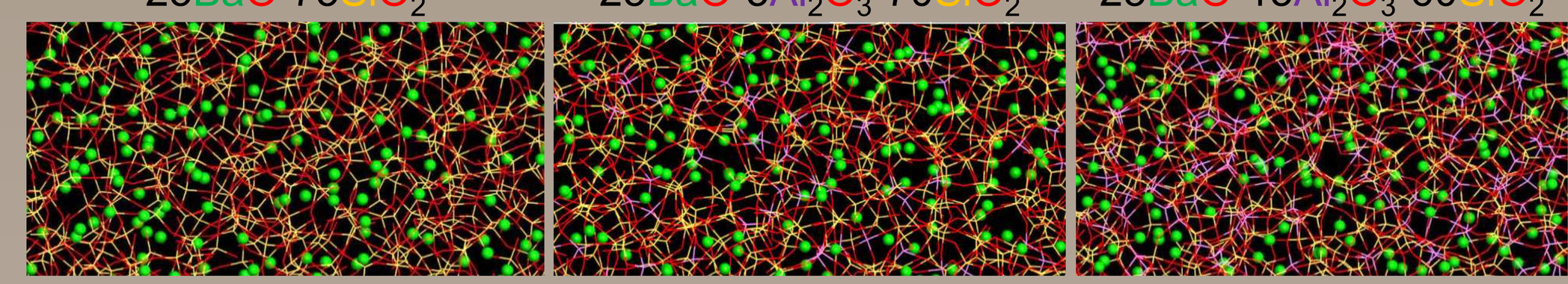
Many sealing glass compositions are based on borosilicate or aluminosilicate compositions

	#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	[illegible]	[illegible]	[illegible]	[illegible]
Aluminum	4	4	5	4	5	22	4	4	4	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Cobalt	0.23	0.23	0.22		0.21		0.24	0.27	0.31	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

XRF of fourteen commercial sealing glasses…. .
All contained significant amounts of Barium.
Other elements can be identified
(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



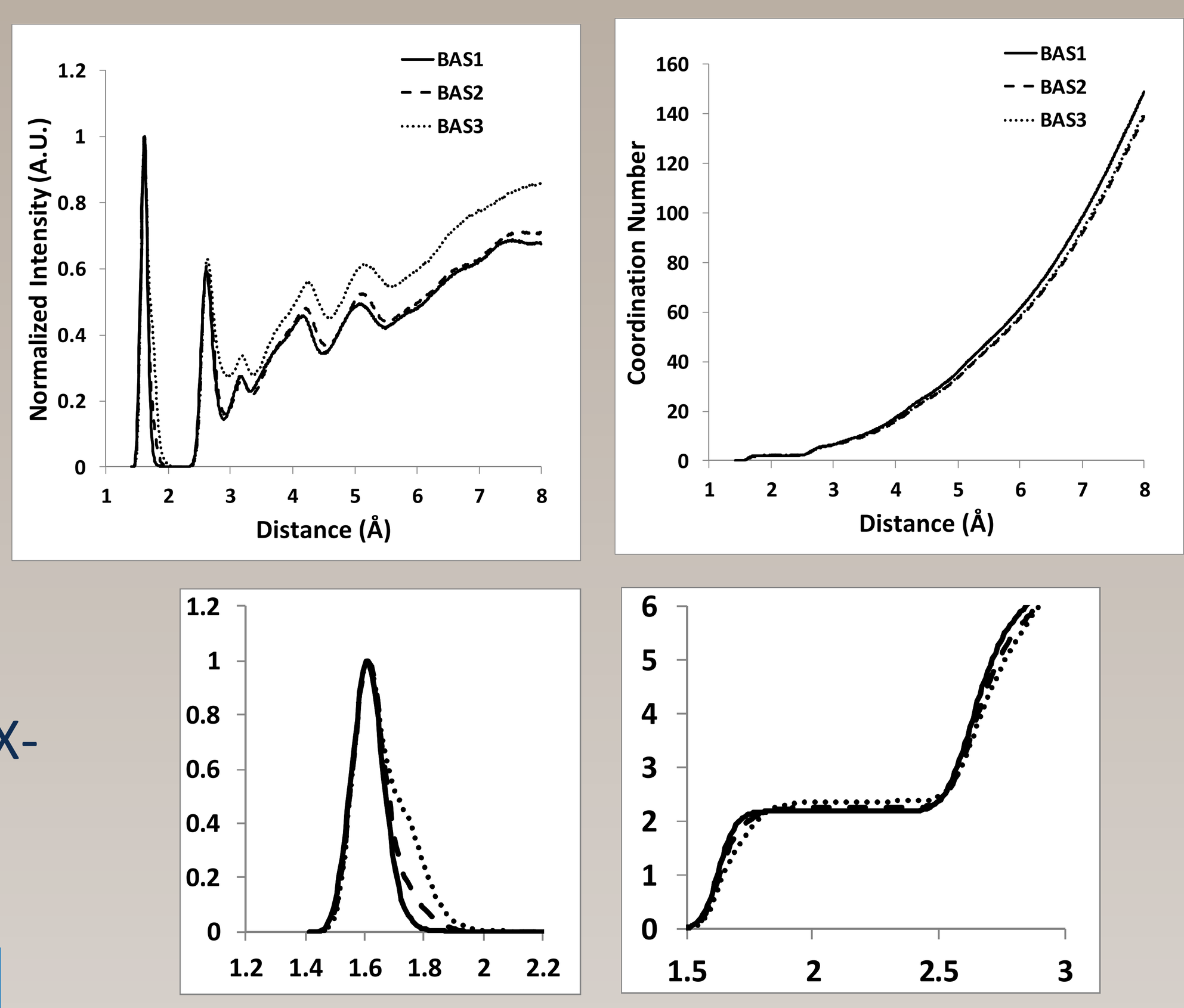
Molecular dynamic calculations have been performed on the model BAS glass formulations

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

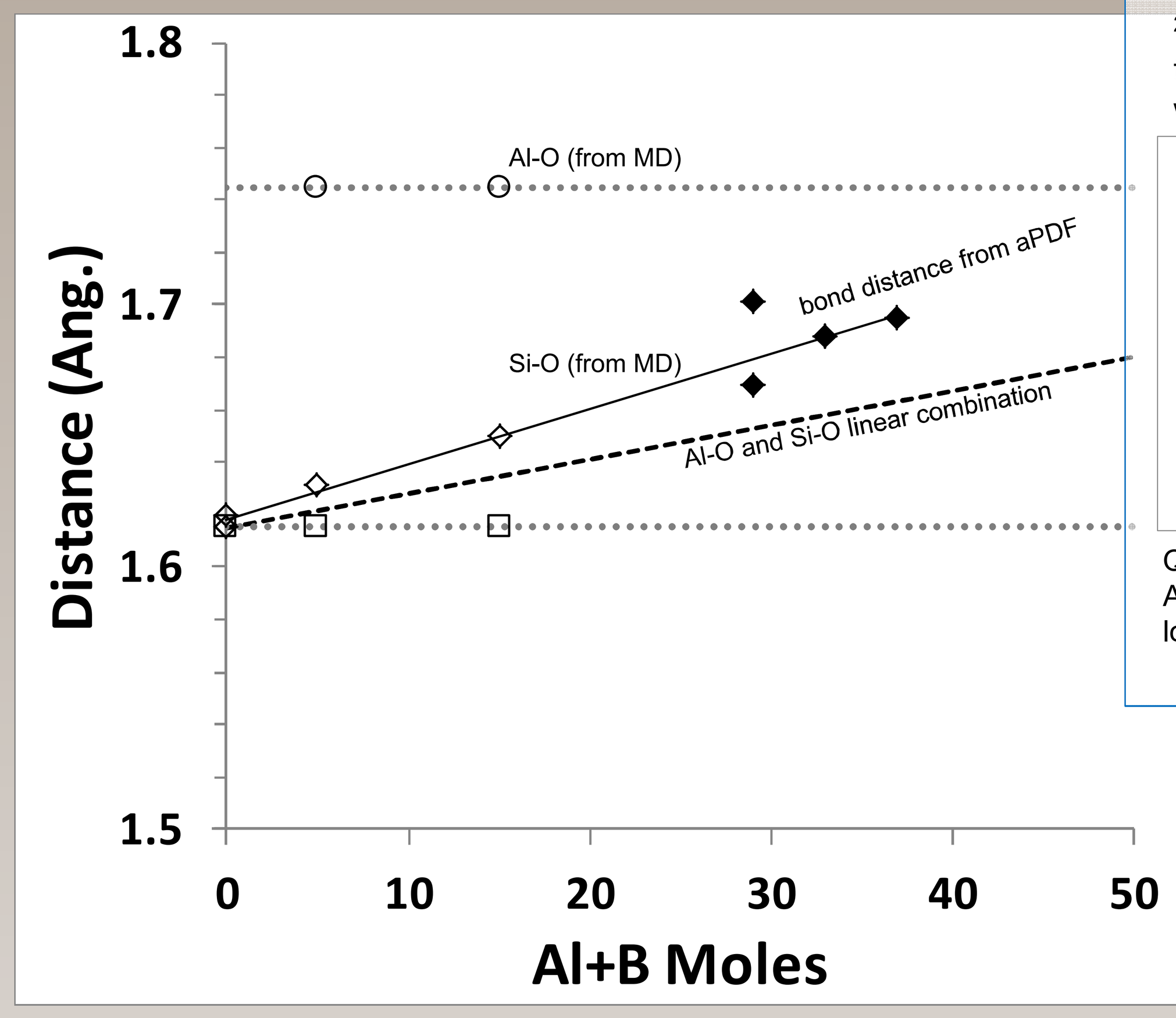
Glass	Oxide Mole %			Archimedes Density (g/cc)	Number of Atoms (in 1x/4x Simulation)					Box Length (Å)
	BaO	Al_2O_3	SiO_2		Ba	Al	Si	O	Total	
BAS 1	25		75	3.52	275/ 1100	0/ 0	825/ 3300	1925/ 7700	3025/ 12100	35.108/ 55.731
BAS 2	25	5	70	3.25	275/ 1100	110/ 440	770/ 3380	1980/ 720	3125/ 12540	36.354/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

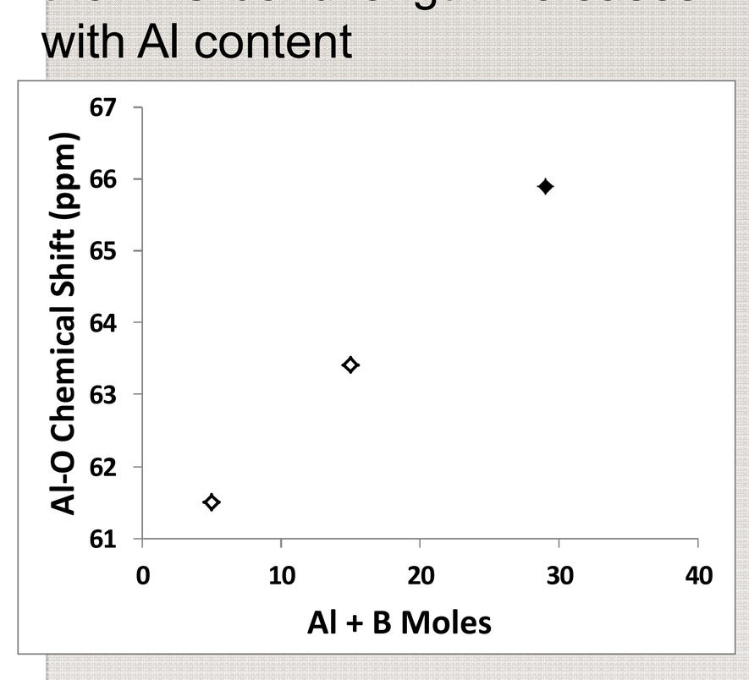


aPDF and MD comparisons show a discrepancy in the 1st nearest neighbor bond length as aluminum is added to the glass composition.



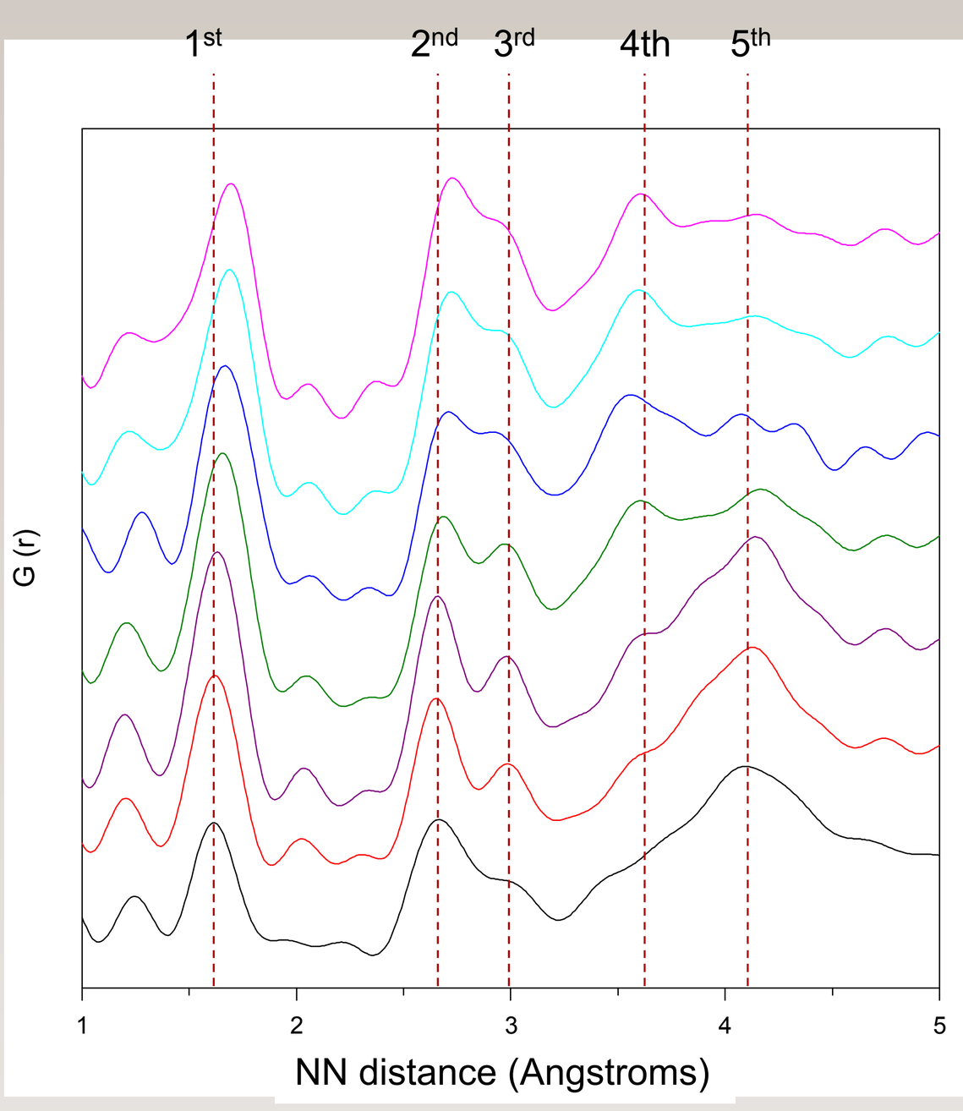
No shifts in Si NMR

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

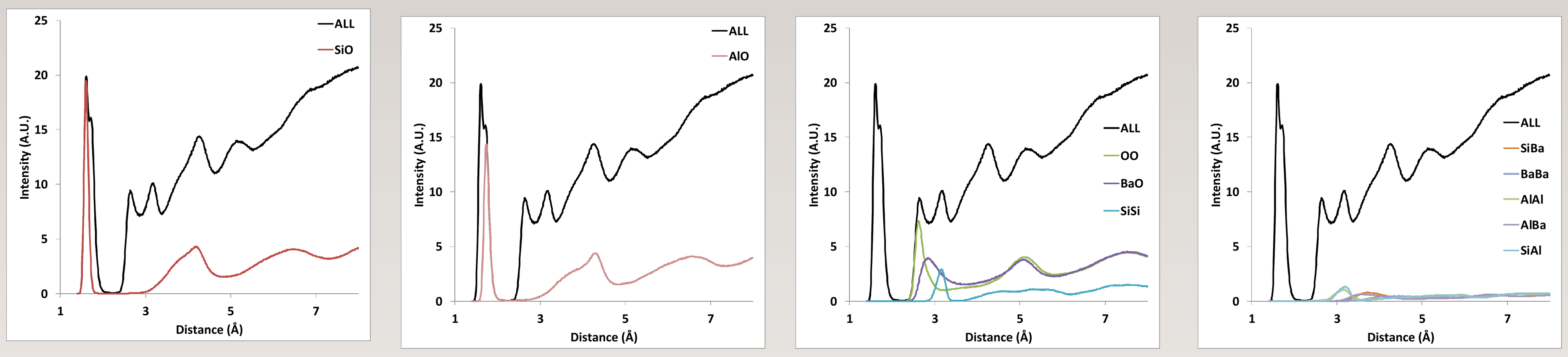


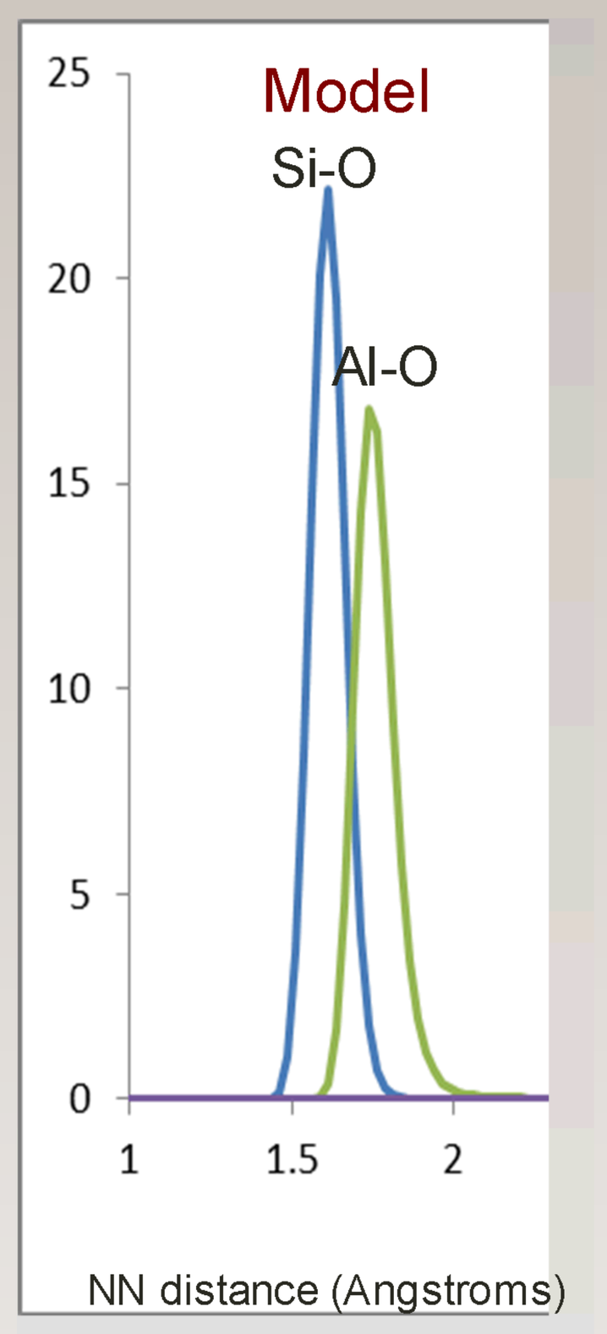
Peak identification supported by MD modeling

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 $Å^{-1}$).

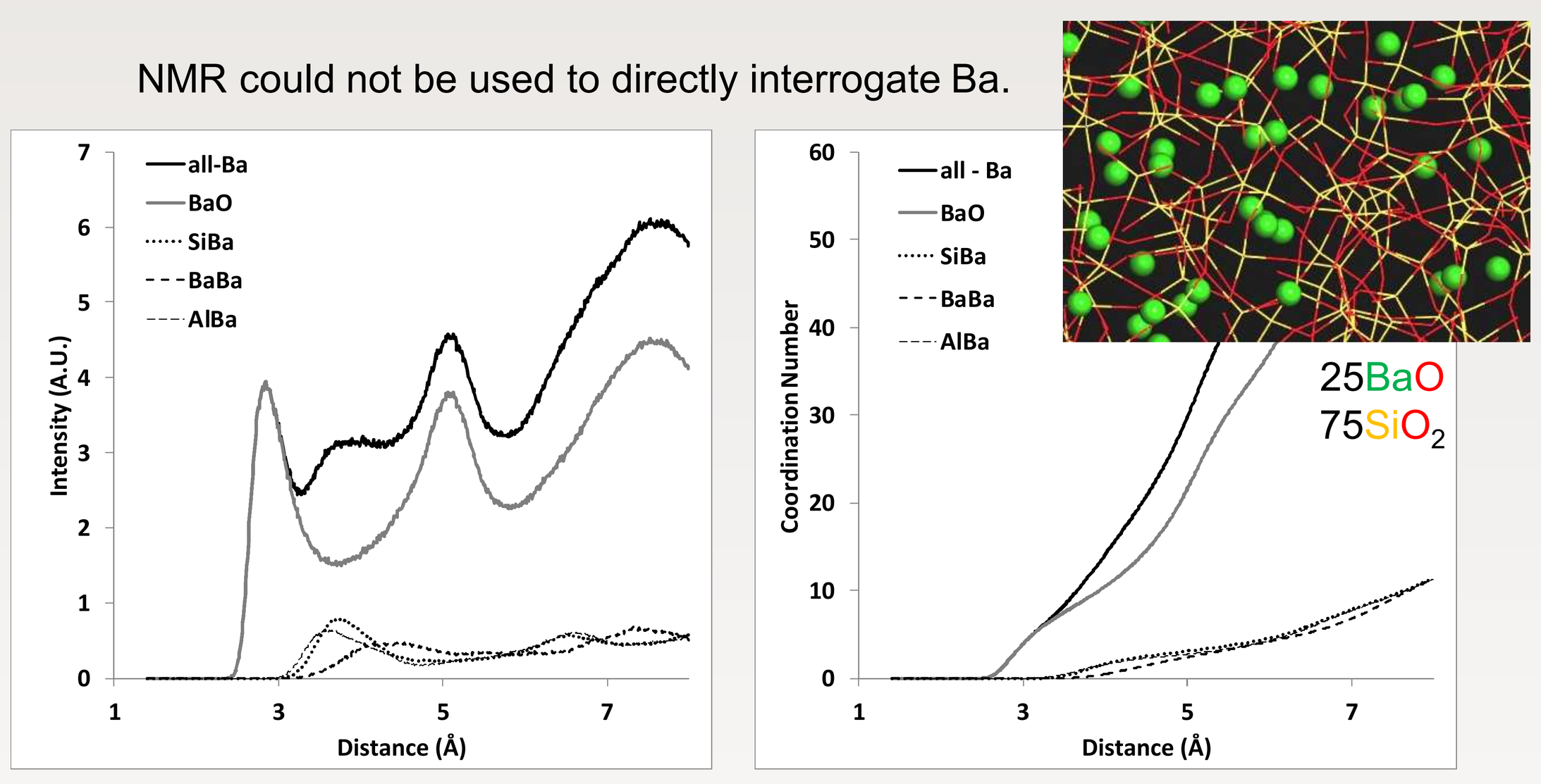
Atom pair bond-lengths are clearly identified from MD





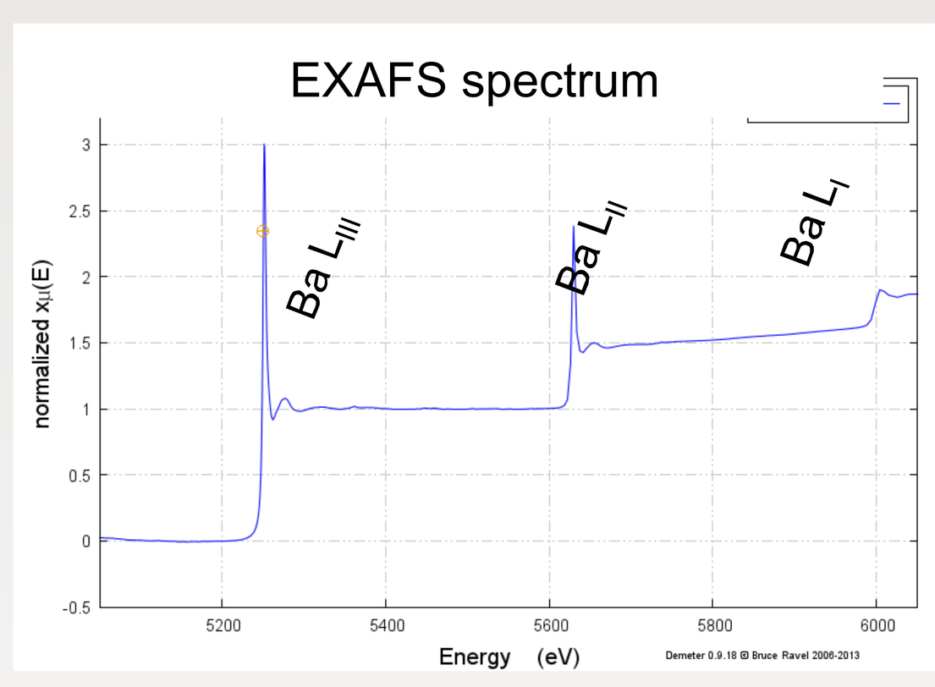
MD shows a long Ba-O bond length and an ill-defined coordination number.

NMR could not be used to directly interrogate Ba.

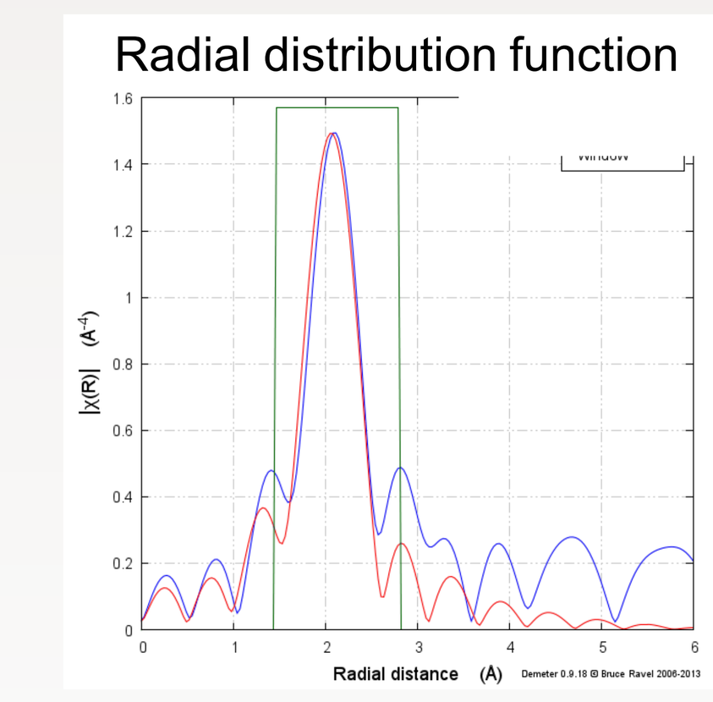


EXAFS was used to corroborate the barium local structure

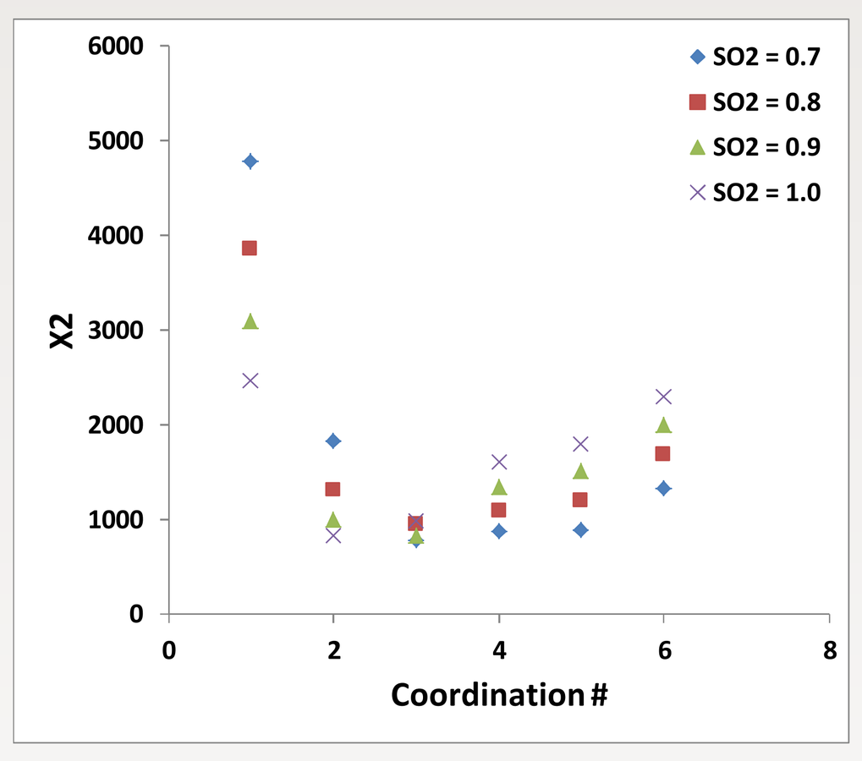
EXAFS spectrum



Radial distribution function

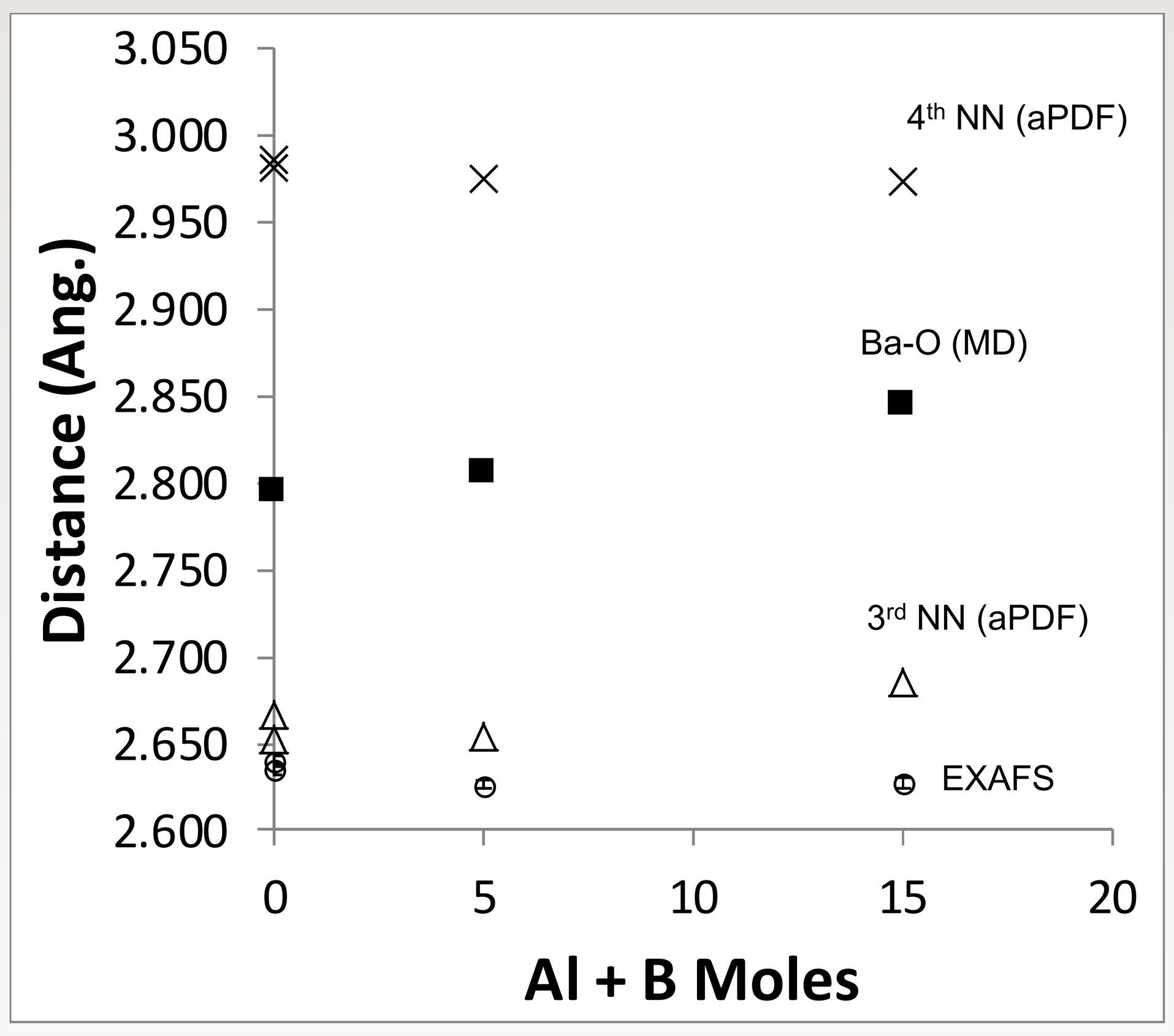


EXAFS fits were relatively insensitive to the coordination number.



Atomic radii (pm)

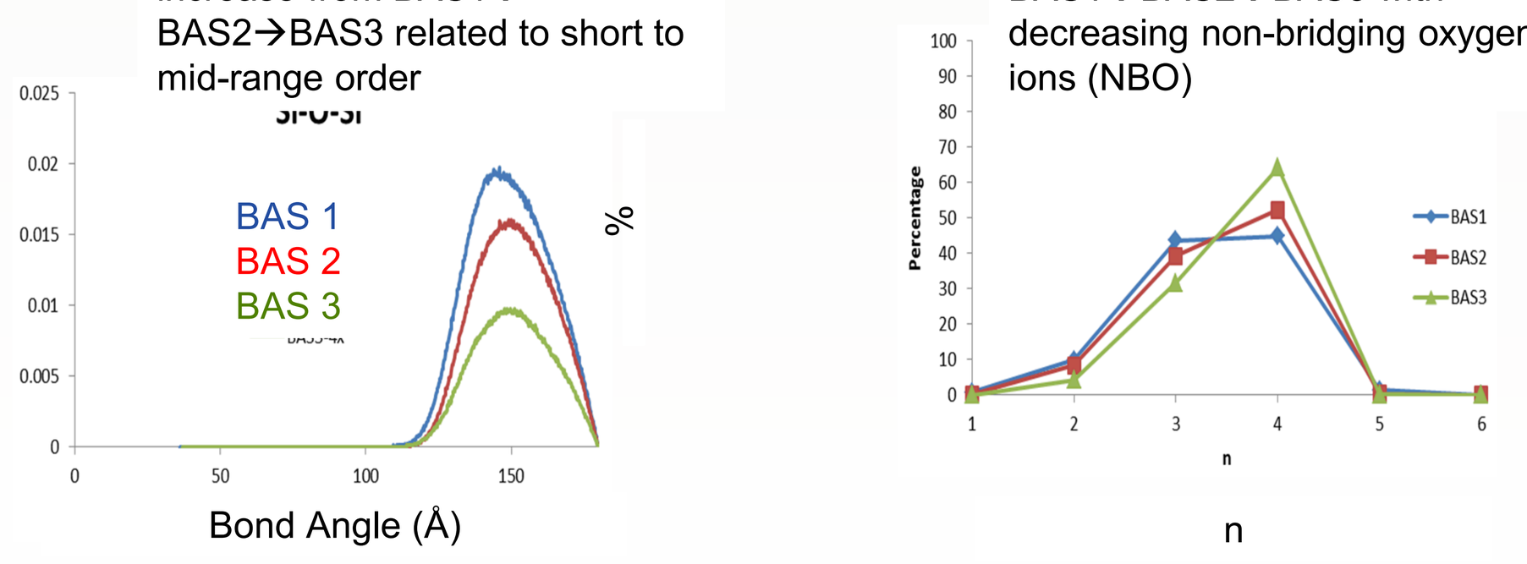
O = 60 Al = 125
B = 85 Ba = 215
Si = 110



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.

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.

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SAND No. 2011-XXXXP

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