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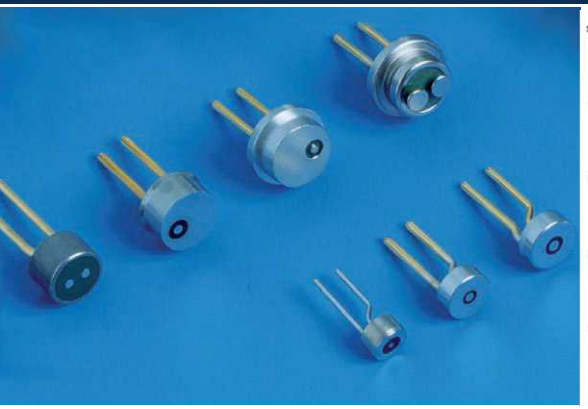

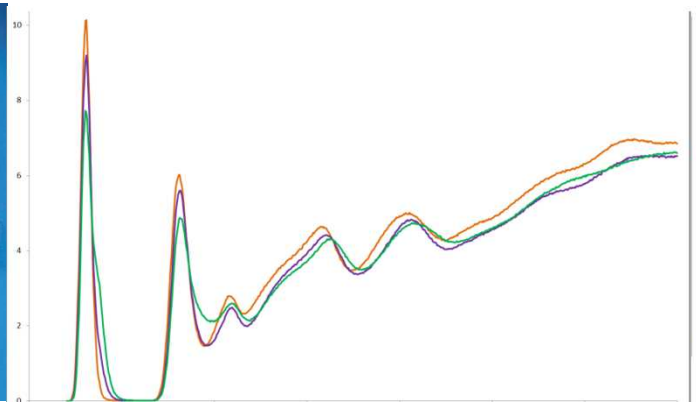

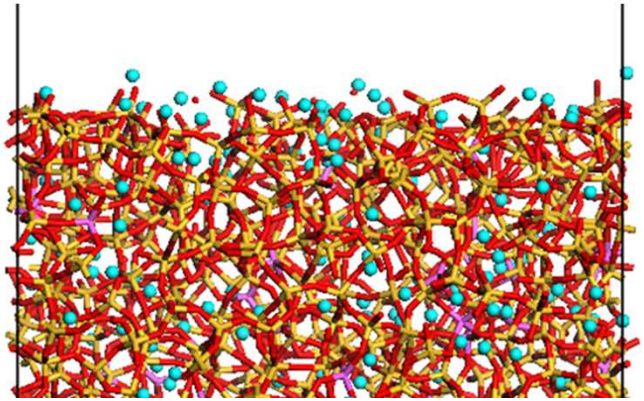

Molecular Dynamics Simulations of Aluminosilicate Sealing Glasses

Todd R. Zeitler, Kevin Ewsuk, Louise Criscenti

9/25/2015

U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

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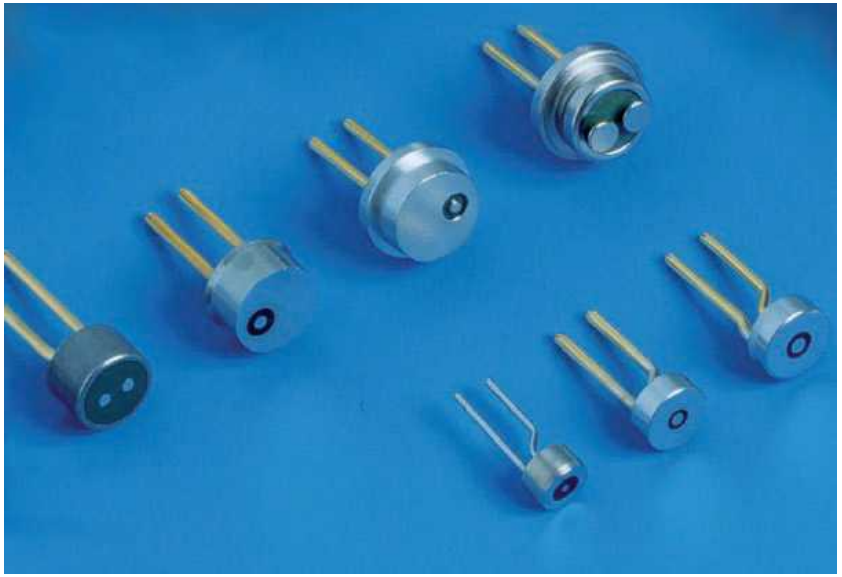
Glass Is Used To Bond/Join Materials

- **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

Feedthroughs for
pressure & flow sensors
(Schott Electronic Packaging)



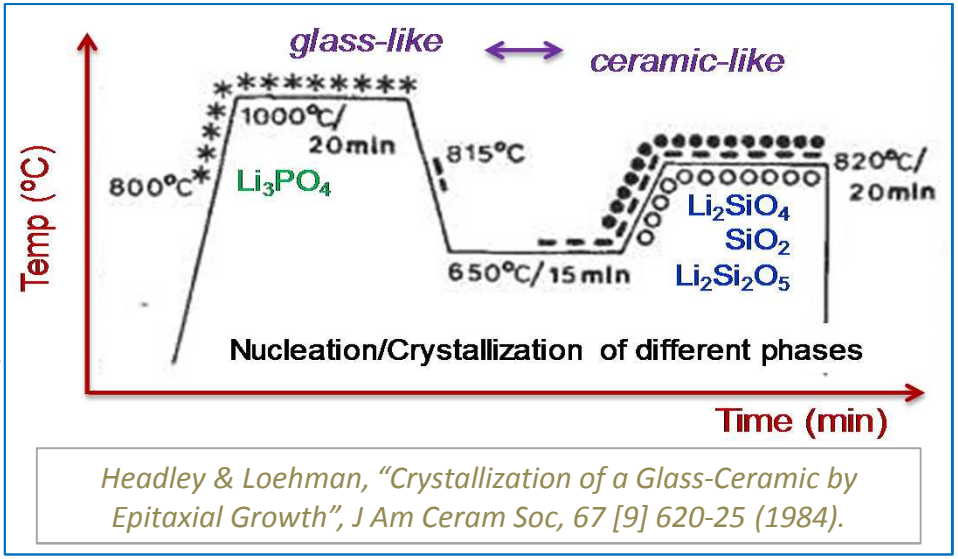
Airbag igniter feedthroughs
(Schott Electronic Packaging)

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

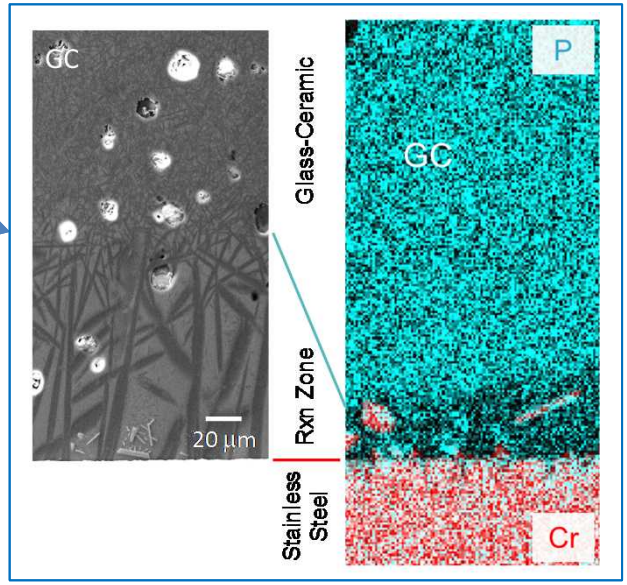
Glass
+ Processability
+ Materials Compatibility
- Low/fixed CTE
- Low toughness/crack tolerance

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).



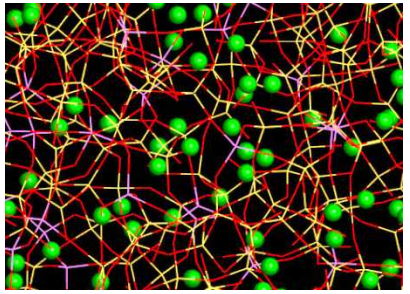
Strategy is to develop FGCs with improved processability and properties

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

Characterization & Modeling Are Being Used To Understand Chemistry-Structure-Property Relations

	Property	Computational Modeling	Experimental Approach	Elemental	Chemical State	Structure
STRUCTURE	bulk structure (glass short-range and medium-range order); surface/interface bond structure	classical MD	MAS-NMR		*	*
			FTIR; Raman		*	*
			XANES; EXAFS; aPDF	*		*
	interface microstructure; devitrification		MAS-NMR		*	*
			XRD			*
			Auger; XPS; SIMS	*	*	*
CHEMISTRY	bulk & interface composition/gradients; diffusion/diffusion profiles	classical MD	Auger; XPS; SIMS	*	*	
			Microprobe; TEM; SEM/EDS	*		
			XRF	*		
	reactivity/reactive sites e.g., hydrolysis of glass bonds	*ab initio* MD; mean force calculations	FTIR / Raman		*	*
			XPS	*	*	*
			NMR		*	*
			NEXAFS	*	*	*
PHYSICAL	glass & composite properties e.g., heat capacity, CTE, viscosity	classical MD; physical models e.g., property & processing	FTIR / Raman		*	
			MAS-NMR		*	*
			Thermal Analysis			
			Wetting/Spreading			

➢ Characterized Glass Chemistry & Structure Using XRF, XPS, EXAFS, aPDFs & NMR.

We Are Developing Experimentally-Validated Modeling To Design/Develop Advanced Filled Glass Composites

- **Objective**
  - Develop experimentally-validated modeling/simulation tools to predict/control glass chemistry-structure-property relations.
- **Approach**
  - Characterize & model glass chemistry-structure-property relations
    - In a simple/model 3 component barium alumino-silicate (BAS) glasses
    - In more complex, commercial-like 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

Molecular Dynamics Simulations

Atomic-scale classical simulations

Born model: point charges

Time evolution of ensemble of ions in simulation box

Thousands of atoms

Ion motion dictated by interatomic potential energy functions and Coulomb energy

$$\mathbf{F}_i = -\nabla_{\mathbf{r}} U = m_i \mathbf{a}$$

Newtonian mechanics

LAMMPS* MD software (open source, developed at Sandia)

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

Pedone* Interatomic Potentials Are Available To Model More Complex Commercial Glass Compositions

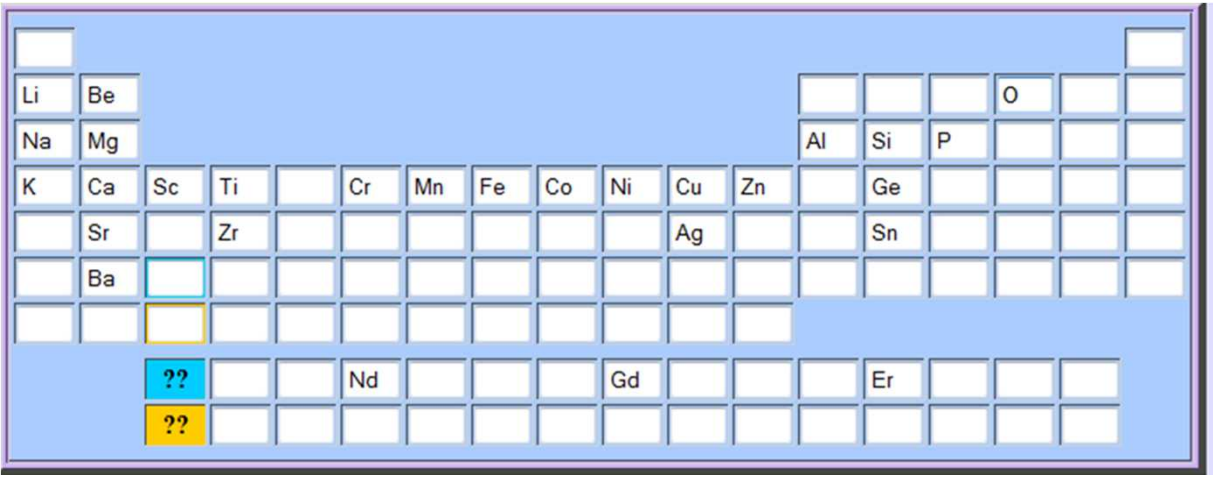


TABLE 2: Potential Parameters of Eq 4 Derived from Binary Oxides[a]

	D_{ij} (eV)	a_{ij} (Å^{-2})	r_0 (Å)	C_{ij} (eV Å^{12})
$Li^{0.6}-O^{-1.2}$	0.001114	3.429506	2.681360	1.0
$Na^{0.6}-O^{-1.2}$	0.023363	1.763867	3.006315	5.0
$K^{0.6}-O^{-1.2}$	0.011612	2.062605	3.305308	5.0
$Be^{1.2}-O^{-1.2}$	0.239919	2.527420	1.815405	1.0
$Mg^{1.2}-O^{-1.2}$	0.038908	2.281000	2.586153	5.0
$Ca^{1.2}-O^{-1.2}$	0.030211	2.241334	2.923245	5.0
$Sr^{1.2}-O^{-1.2}$	0.019623	1.886000	3.328330	3.0
$Ba^{1.2}-O^{-1.2}$	0.065011	1.547596	3.393410	5.0
$Sc^{1.8}-O^{-1.2}$	0.000333	3.144445	3.200000	2.6
$Ti^{2.4}-O^{-1.2}$	0.024235	2.254703	2.708943	1.0
$Zr^{2.4}-O^{-1.2}$	0.206237	2.479675	2.436997	1.0
$Cr^{1.8}-O^{-1.2}$	0.399561	1.785079	2.340810	1.0
$Mn^{1.2}-O^{-1.2}$	0.029658	1.997543	2.852075	3.0
$Fe^{1.2}-O^{-1.2}$	0.078171	1.822638	2.658163	2.0
$Fe^{1.8}-O^{-1.2}$	0.418981	1.620376	2.382183	2.0
$Co^{1.2}-O^{-1.2}$	0.012958	2.361272	2.756282	3.0
$Ni^{1.2}-O^{-1.2}$	0.029356	2.679137	2.500754	3.0
$Cu^{0.6}-O^{-1.2}$	0.090720	3.802168	2.055405	1.0
$Ag^{0.6}-O^{-1.2}$	0.088423	3.439162	2.265956	1.0
$Zn^{1.2}-O^{-1.2}$	0.001221	3.150679	2.851850	1.0
$Al^{1.8}-O^{-1.2}$	0.361581	1.900442	2.164818	0.9
$Si^{2.4}-O^{-1.2}$	0.340554	2.006700	2.100000	1.0
$Ge^{2.4}-O^{-1.2}$	0.158118	2.294230	2.261313	5.0
$Sn^{2.4}-O^{-1.2}$	0.079400	2.156770	2.633076	3.0
$P^{3.0}-O^{-1.2}$	0.831326	2.585833	1.800790	1.0
$Nd^{1.8}-O^{-1.2}$	0.014580	1.825100	3.398717	3.0
$Gd^{1.8}-O^{-1.2}$	0.000132	2.013000	4.351589	3.0
$Er^{1.8}-O^{-1.2}$	0.040448	2.294078	2.837722	3.0
$O^{-1.2}-O^{-1.2}$	0.042395	1.379316	3.618701	22.0[b]

*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).

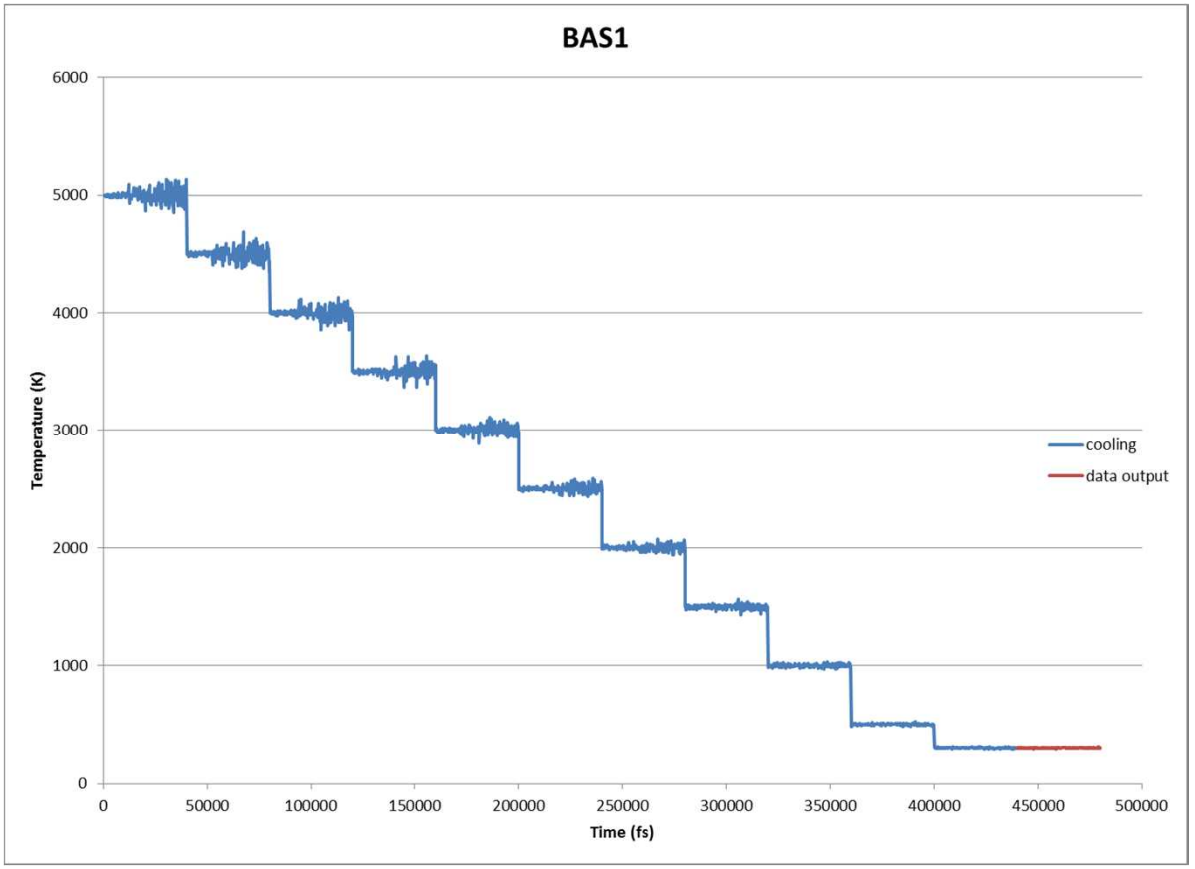
Typical Stepped Annealing Schedule

Glass creation schedule:

stage	T (K)	steps	time (ps)	ensemble
1	5000	20000	40	NVT
2	4500	20000	40	NVT
3	4000	20000	40	NVT
4	3500	20000	40	NVT
5	3000	20000	40	NVT
6	2500	20000	40	NVT
7	2000	20000	40	NVT
8	1500	20000	40	NVT
9	1000	20000	40	NVT
10	500	20000	40	NVT
11	300	20000	40	NVT
12	300	20000	40	NVE

Data taken over NVE step.

Each of first 11 steps consists of three steps: 1) 6000 steps with velocity scaling every step; 2) 6000 steps with v.s. every 40 steps; 3) 8000 steps with no v.s.

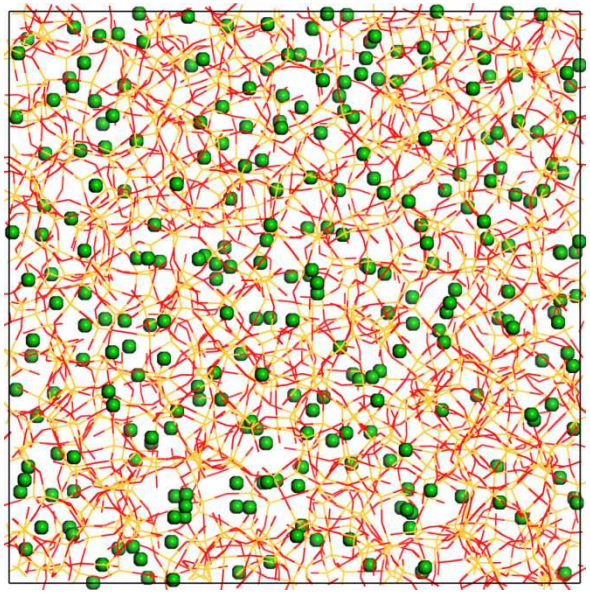


Three Simulated Glass Structures

$$25\ BaO - X\ Al_2O_3 - (75\text{-}x)\ SiO_2$$

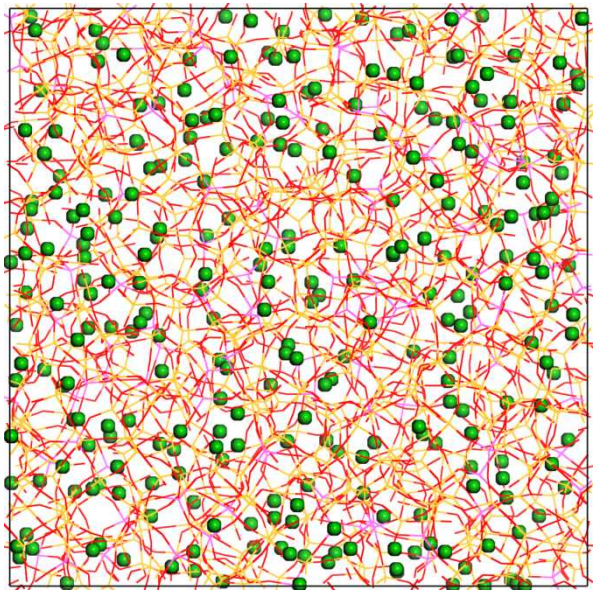
BAS 1

25 BaO - 75 SiO_2



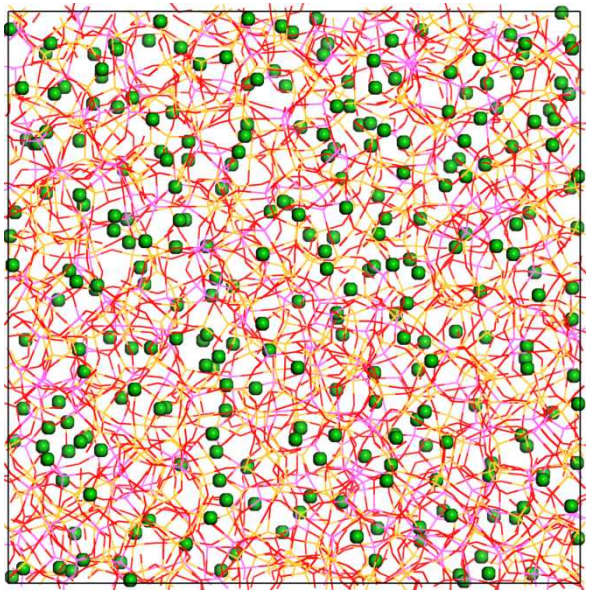
BAS 2

25 BaO - 5 Al_2O_3 - 70 SiO_2



BAS 3

25 BaO - 15 Al_2O_3 - 60 SiO_2



Tabulated results for the three compositions

	Composition (mol%)										CTE (x 10^{-6} K^{-1})					
	SiO_2	Al_2O_3	BaO	B_2O_3	NBO_{theo} (%)	NBO_{MD} (%)	$Connectivity_{theo}$ (BO/NF)	$Density_{SG}$ (g/cm^3)	$Density_{MD}$ (g/cm^3)	±	low	±	high	±	T_g (K)	±
BAS1	75		25		28.6	28.0	1.67	3.29	3.31	0.01	11.6	0.5	31.0	6.3	1710	95
BAS2	70	5	25		22.2	22.1	1.75	3.31	3.32	0.02	10.4	0.6	24.1	6.1	1638	225
BAS3	60	15	25		10.5	13.6	1.89	3.33	3.39	0.01	10.1	0.4	19.1	4.2	1667	116

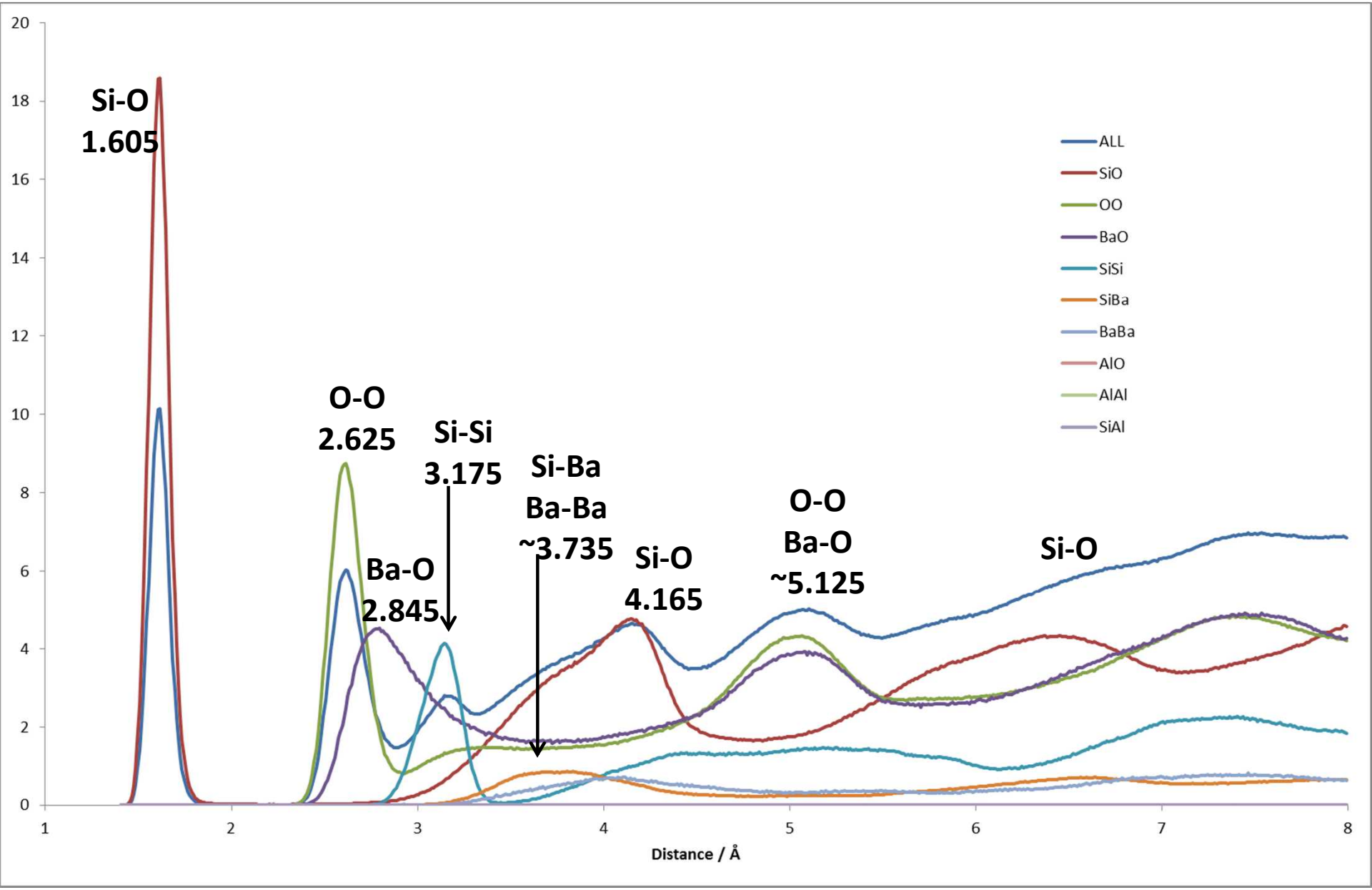
The MD density values are pretty close to the SciGlass calculated and show the slight increase that the SciGlass values show. Our experimental values show the opposite trend. All of the structural results we looked at previously were calculated based on the experimental density measurements.

The CTE shows a decrease, which is consistent with the higher connectivity structures created by the added alumina.

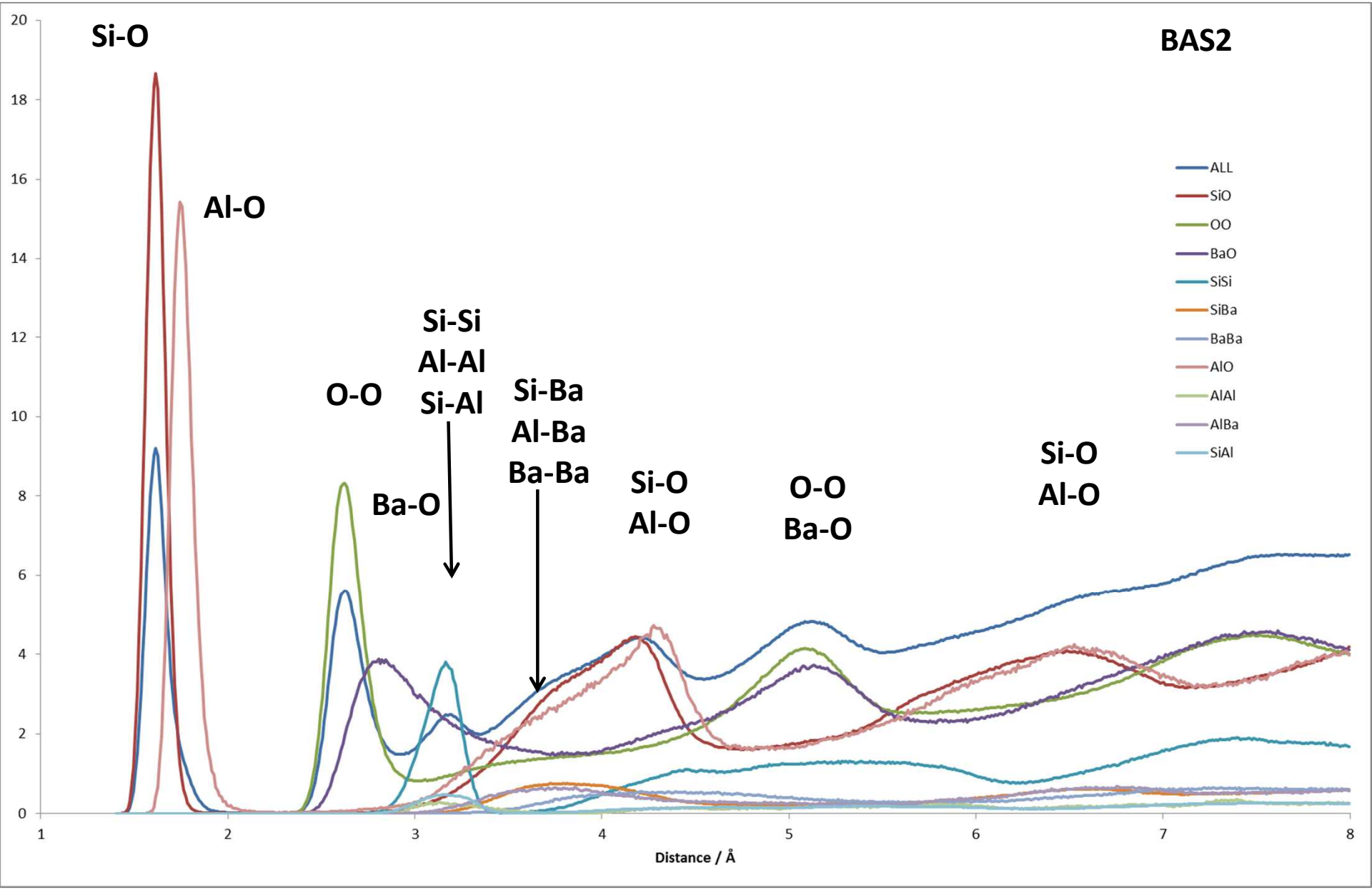
It's difficult to make much of the Tg values, since the errors are so great. They are all relatively high, which is typical for MD-created structures. The averaged curves look OK, but the individual heating curves have a lot of variance.

Non-bridging oxygen (NBO) content matches theoretical calculations well.

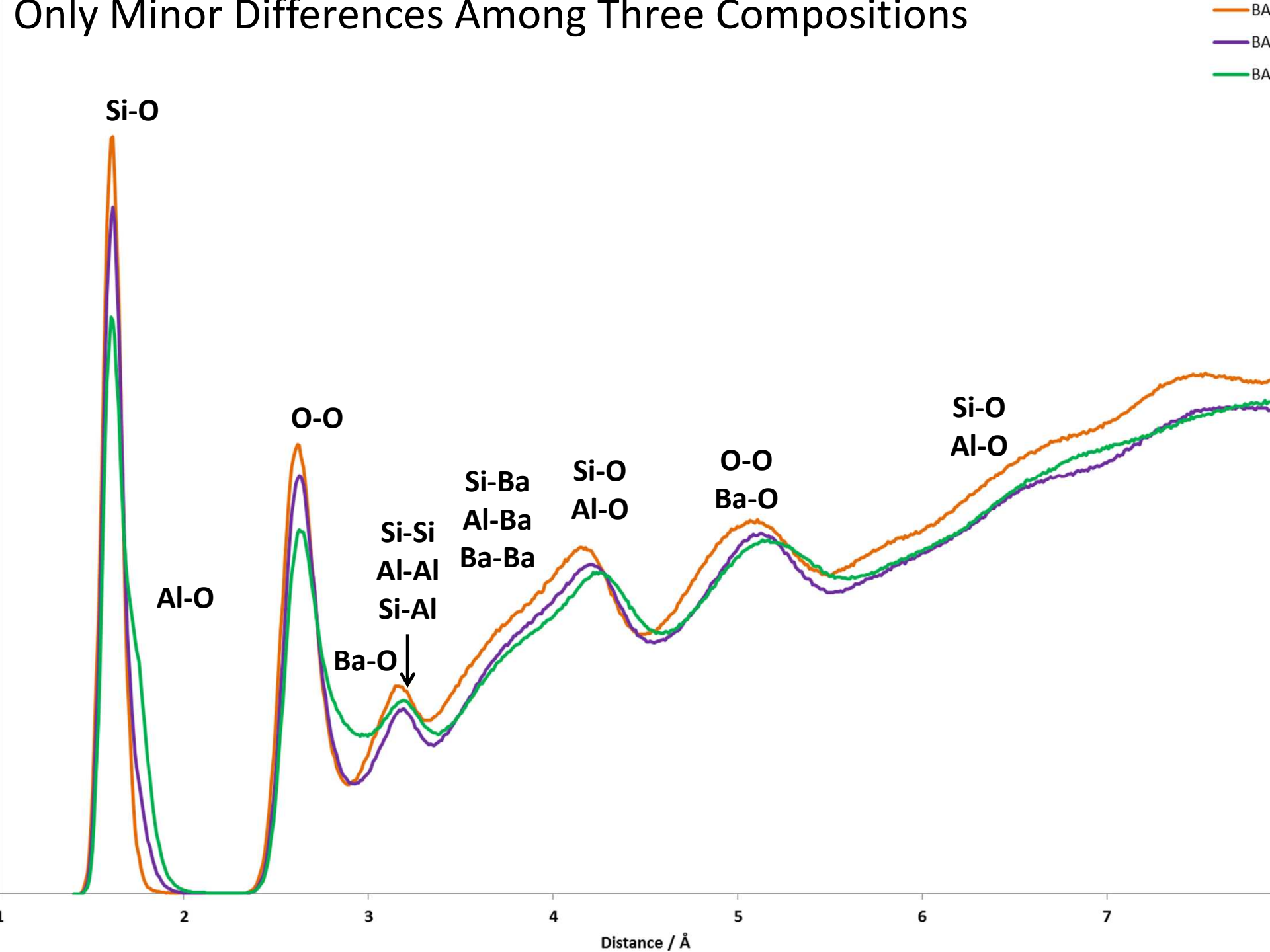
BAS1


Si-O
1.605
O-O
2.625
Ba-O
2.845
Si-Si
3.175
Si-Ba
Ba-Ba
~3.735
Si-O
4.165
O-O
Ba-O
~5.125
Si-O
ALL
SiO
OO
BaO
SiSi
SiBa
BaBa
AlO
AlAl
SiAl
Distance / Å

Typical Radial Distribution Function



Only Minor Differences Among Three Compositions



Few Structural Defects in Bulk Glass Simulations

Si and Al almost exclusively 4-coordinated

Si Coordination

Glass	4-coord	5-coord	6-coord
BAS1	98.7	1.3	0.0
BAS2	99.7	0.3	0.0
BAS3	99.9	0.1	0.0

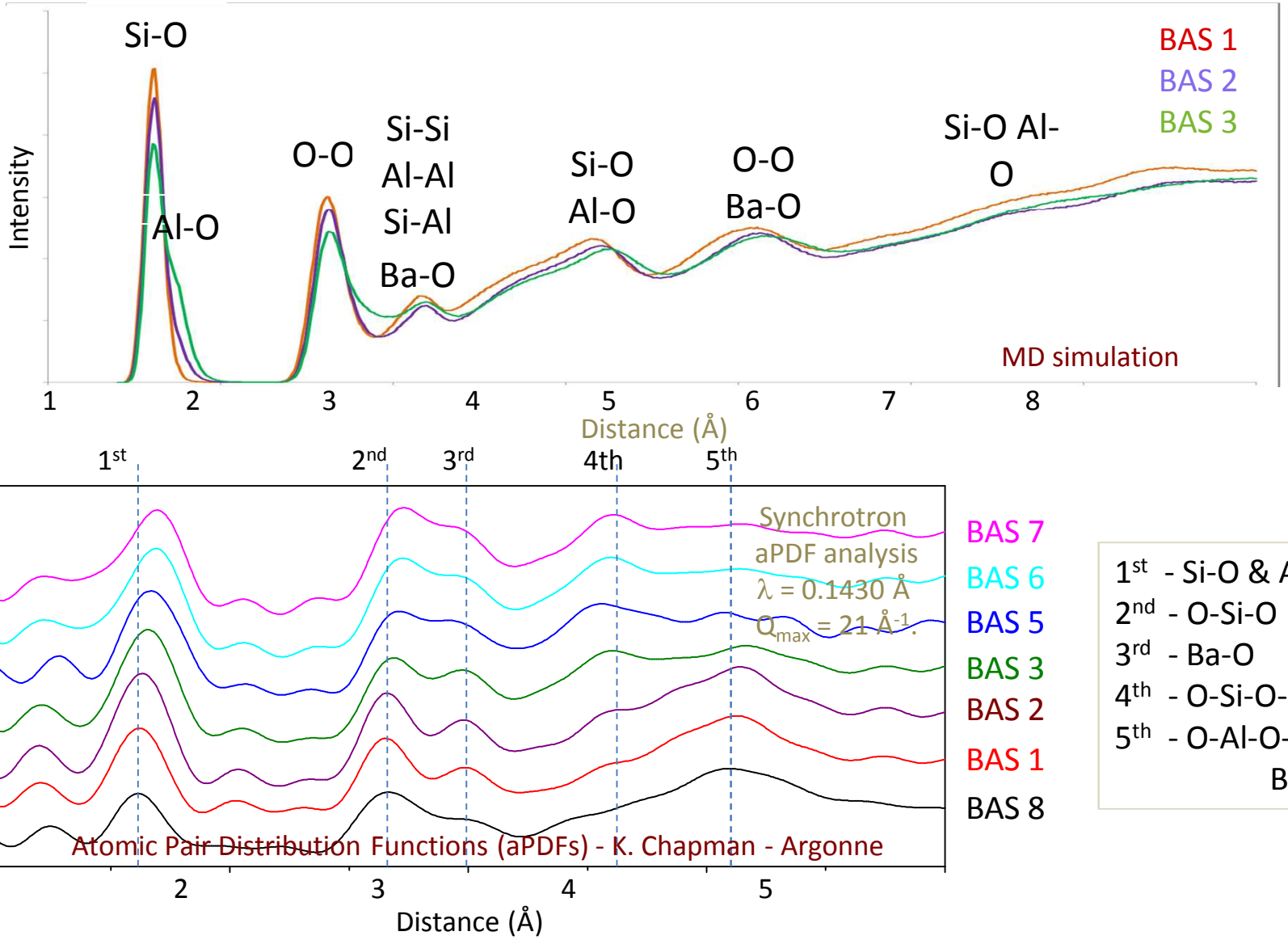
Al Coordination

Glass	3-coord	4-coord	5-coord	6-coord
BAS1	-	-	-	-
BAS2	0.0	96.8	3.2	0.0
BAS3	0.2	97.1	2.6	0.1

Peak positions are invariant to composition

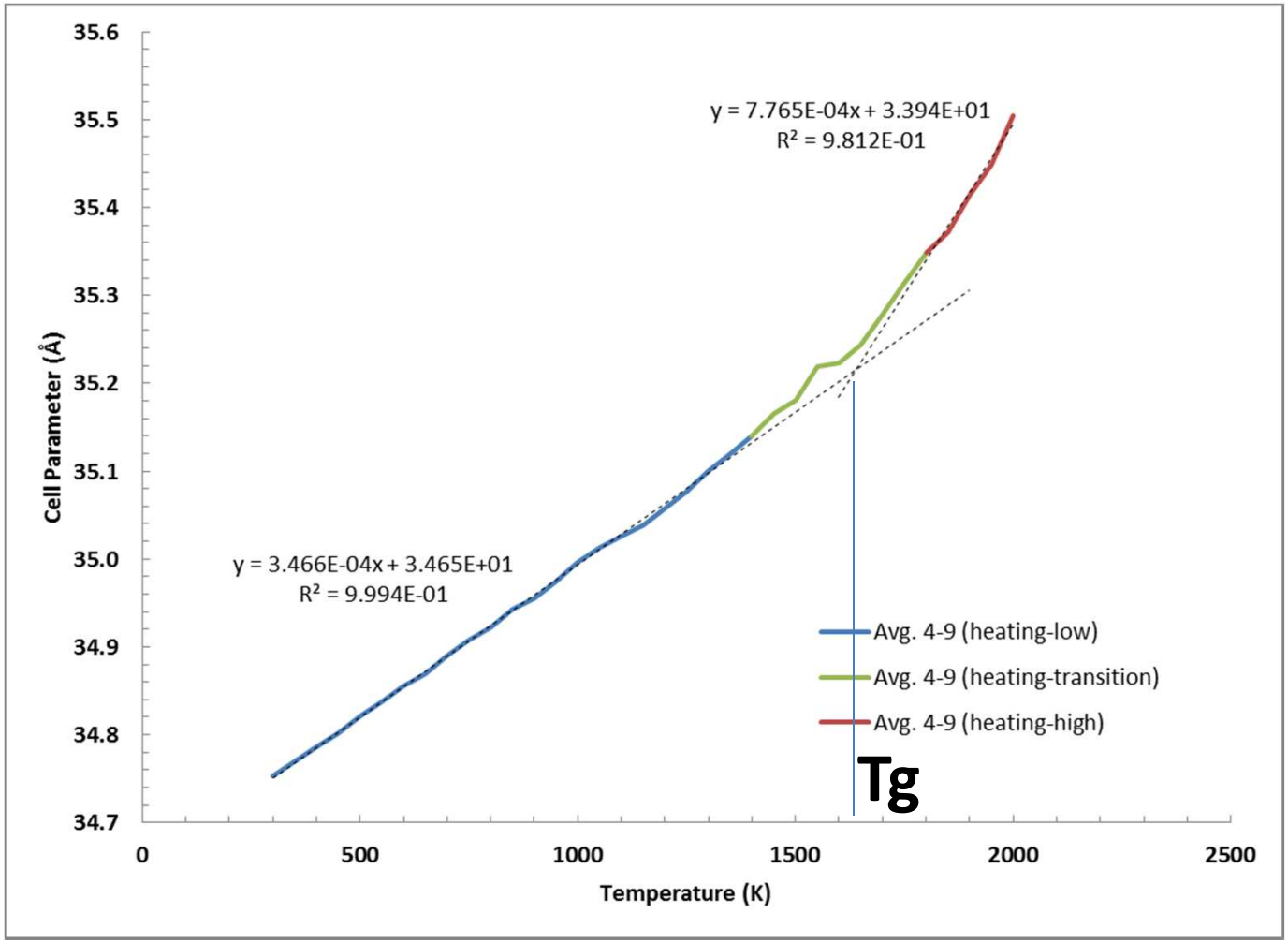
First Network Former Peak	Si			Al		
Glass	Total	BO	NBO	Total	BO	NBO
BAS1	1.62	1.62	1.55	-	-	-
BAS2	1.62	1.62	1.56	1.75	1.75	1.70
BAS3	1.61	1.62	1.56	1.75	1.74	1.70

Measured aPDF Peaks Are Consistent With Nearest Neighbor (NN) Distances From 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

CTE calculated below and above Tg



*Stechert, et al. *J. Non-Cryst. Solids* **2012,** *358* (16), 1917-1923.

Sealing Glass Simulation Setup – 6 and 7-Component Systems

Original compositions (don't all add to 100%)

From Table in Paper

wt%

Glass Name	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	%check Total
TM9	66.82	3.51	12.02	0.11		7.24	7.21		0.62		0.02	0.13	0.07	0.6					98.35
Sch8061	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
Cor9013	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
EG2164	64.26	2.36	13.8	0.36	2.84	7.18	6.35	0.01	2.57	0.14	0.13								100.00
Cor9010	64.4	4.4		0.2		7.2	9.3			0.1				0.5					86.10

Drop components with < mol 1%

wt%

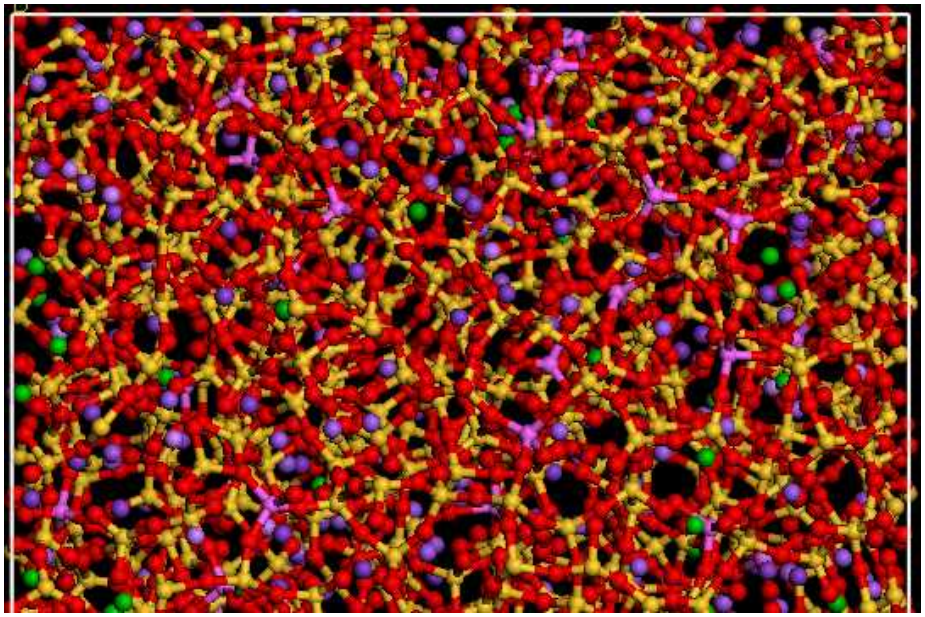
Glass Name	SiO_2	Al_2O_3	BaO	CaO	B_2O_3	Na_2O	K_2O	PbO	Li_2O	MgO	SrO	CoO	Fe_2O_3	Sb_2O_3	ZrO_2	Cr_2O_3	Sr_2O_3	HfO_2	%check Total
TM9	66.82	3.51	12.02			7.24	7.21		0.62										97.42
Sch8061	68.8	3.59	11			7.02	7.46		0.74										98.61
Cor9013	65.63	3.38	12.3			7.39	5.87		0.688						1.756				97.01
EG2164	64.26	2.36	13.8			7.18	6.35		2.57										96.52
Cor9010	64.4	4.4				7.2	9.3												85.30

Actual wt% after resetting to 100 wt% (compositions aren't very different)

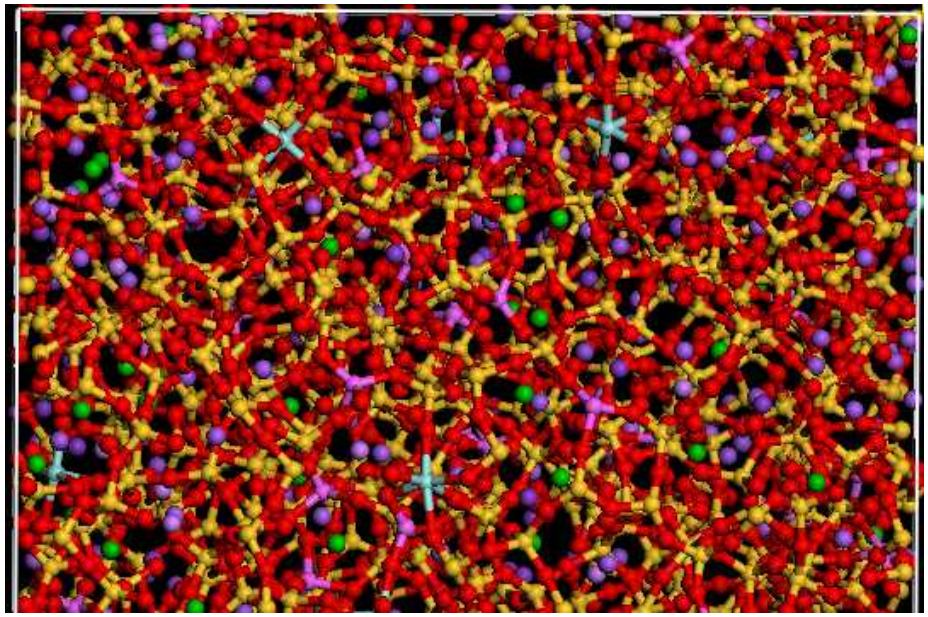
Actual wt%

Glass Name	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
TM9	68.6	3.6	12.4			7.4	7.5		0.6										100.00
Sch8061	69.8	3.6	11.2			7.1	7.5		0.8										100.00
Cor9013	67.6	3.5	12.7			7.6	6.0		0.7						1.8				100.00
EG2164	66.6	2.5	14.3			7.5	6.6		2.7										100.00
Cor9010	75.4	5.2				8.4	10.9												100.00

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



T-1

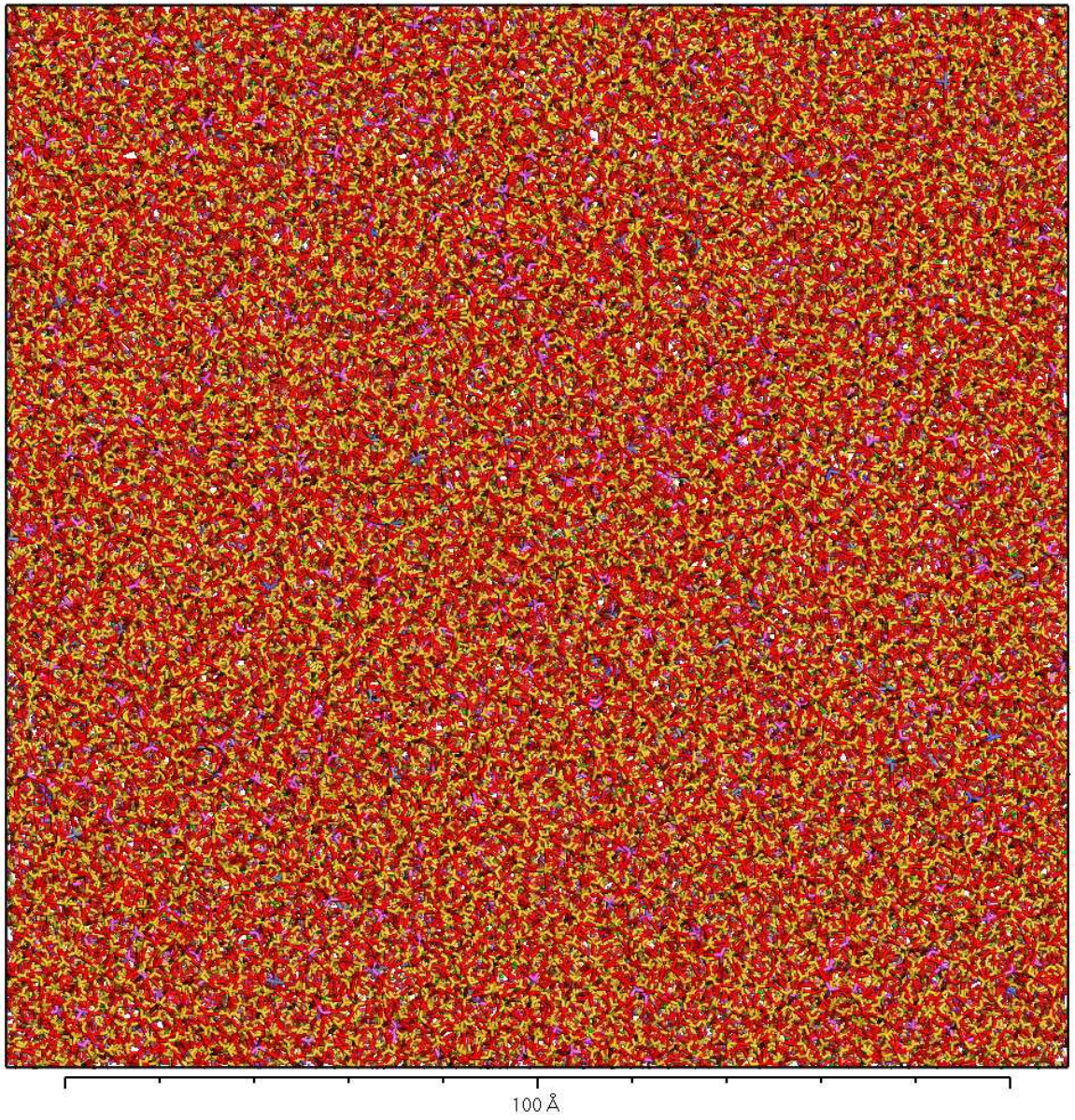


C-1

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

T. Zeitler

Larger Systems are Needed to get Good Statistics for Smaller Components



S1-30x (final configuration)

Si	Al	Ba	Ca	B	Na	K	Pb	Li	Mg	Sr	Co	Fe	Sb	Zr	Cr	Sr	Hf	O	Total
25598	1574	1604			5064	3540		1108	24		39	64			120			60356	99091

Have begun Surface Simulations in Preparation for Interface Simulations

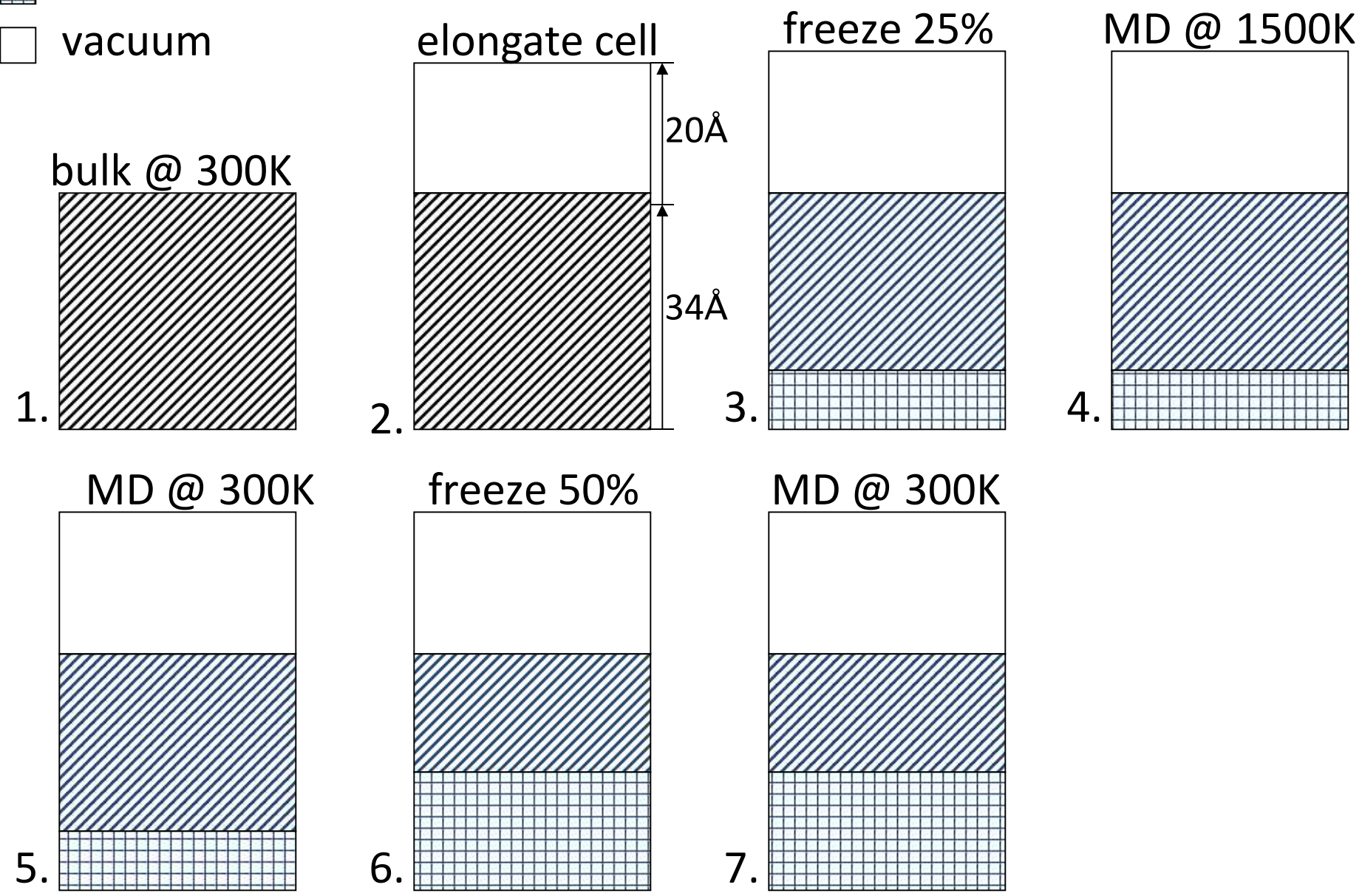
Glass Compositions (mol %) for surface investigation

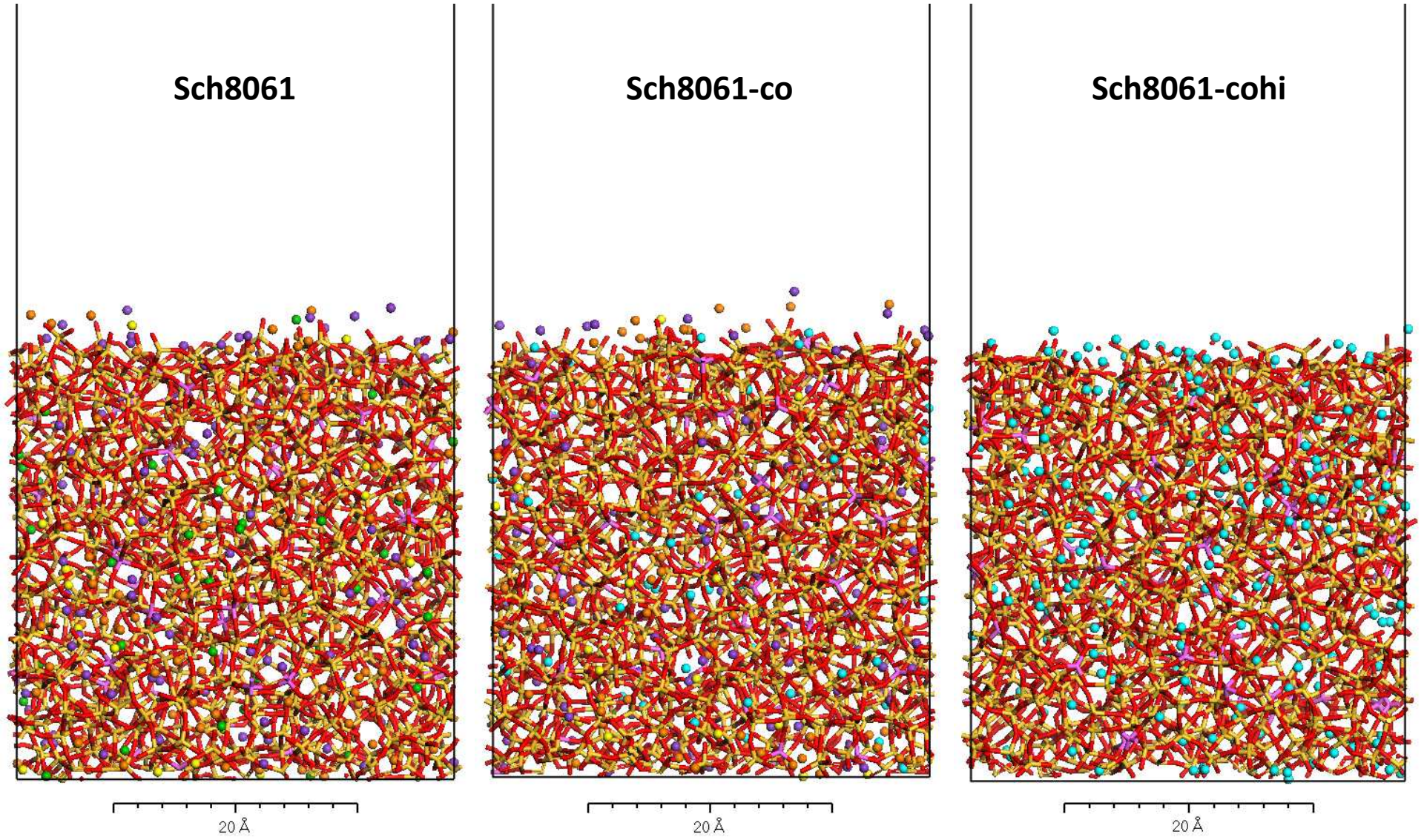
Glass	SiO_2	Al_2O_3	BaO	Na_2O	K_2O	Li_2O	CoO	
Sch8061	77.9	2.4	4.9	7.7	5.4	1.7		**Initial composition**
Sch8061-co	77.9	2.4		7.7	5.4	1.7	4.9	**Replace BaO with CoO**
Sch8061-cohi	77.9	2.4					19.6	**Replace all modifiers with CoO**

Experimentally, Co is observed to accumulate at the surface

mobile
immobile
vacuum

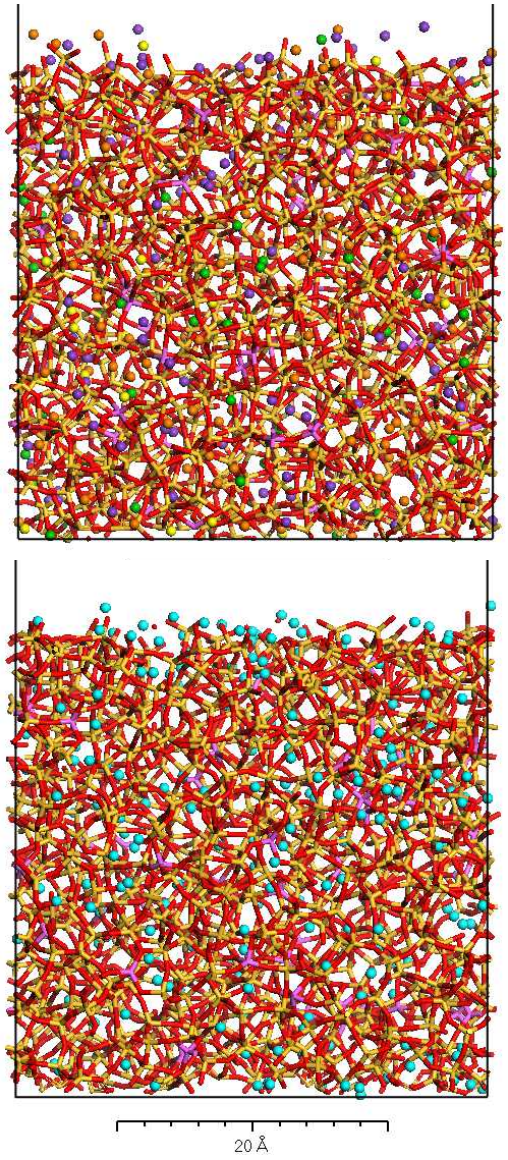
Typical MD Glass Surface Simulation (after Garofalini)

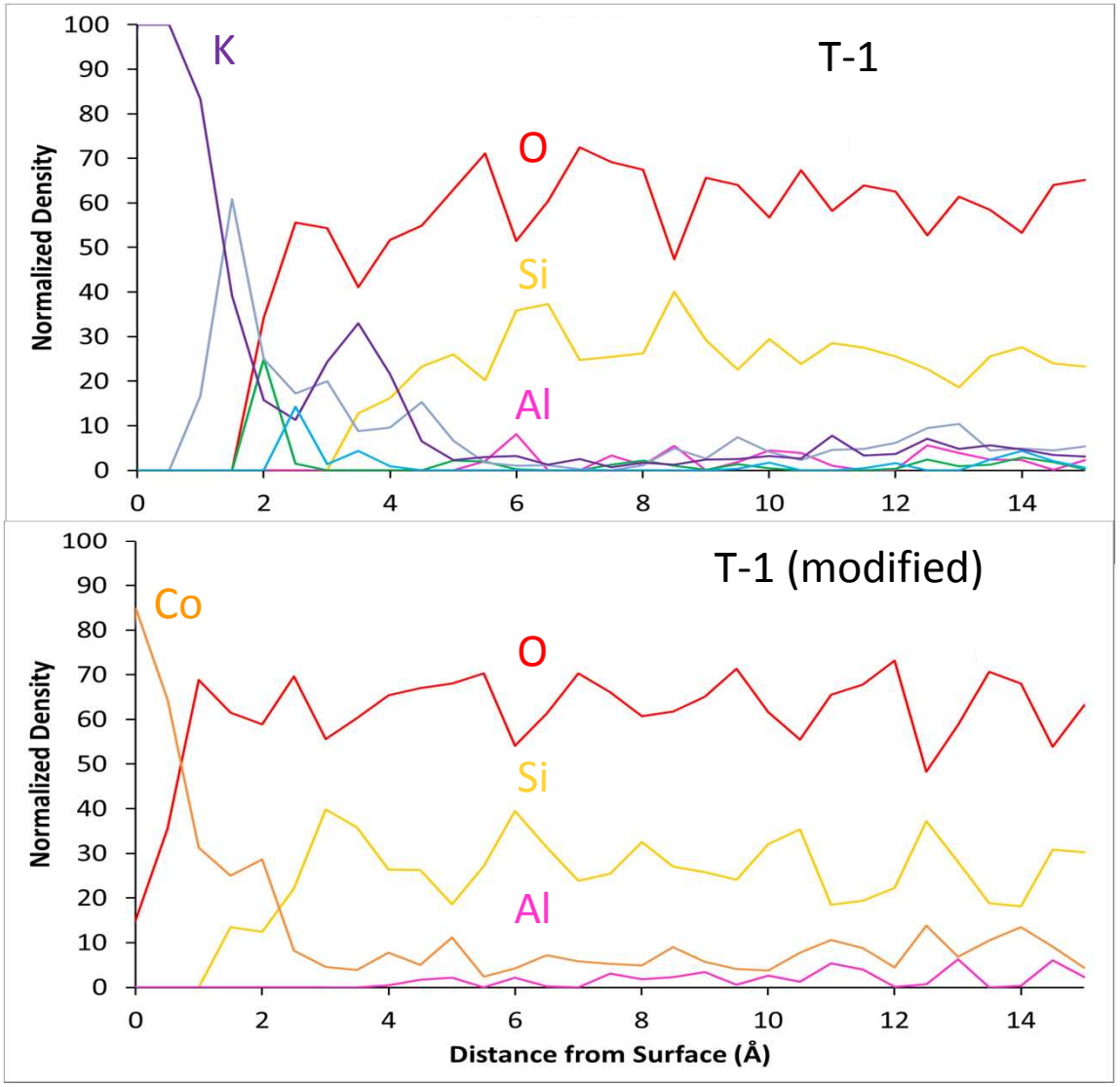




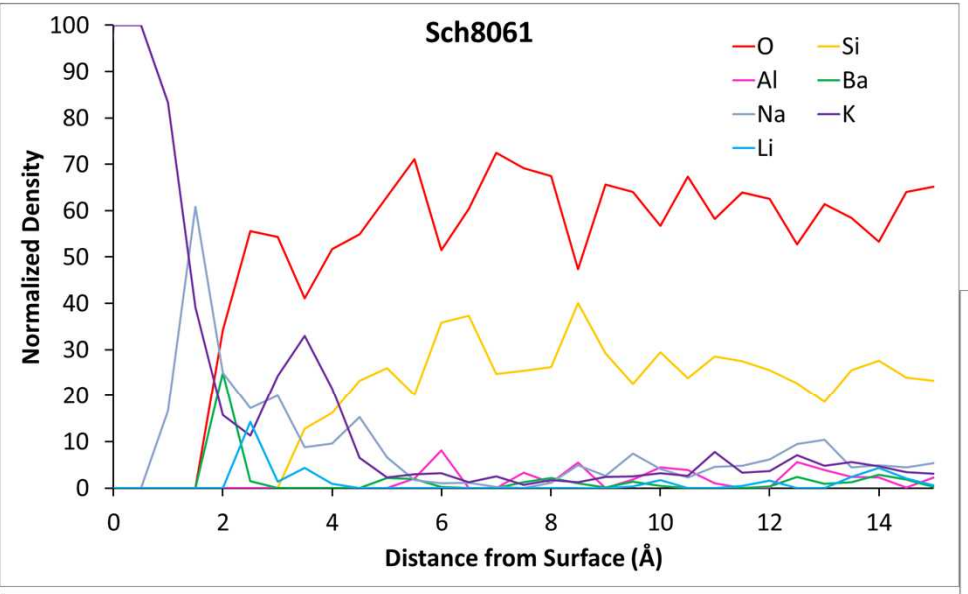
Si, Al, O, Ba, Na, K, Li, Co

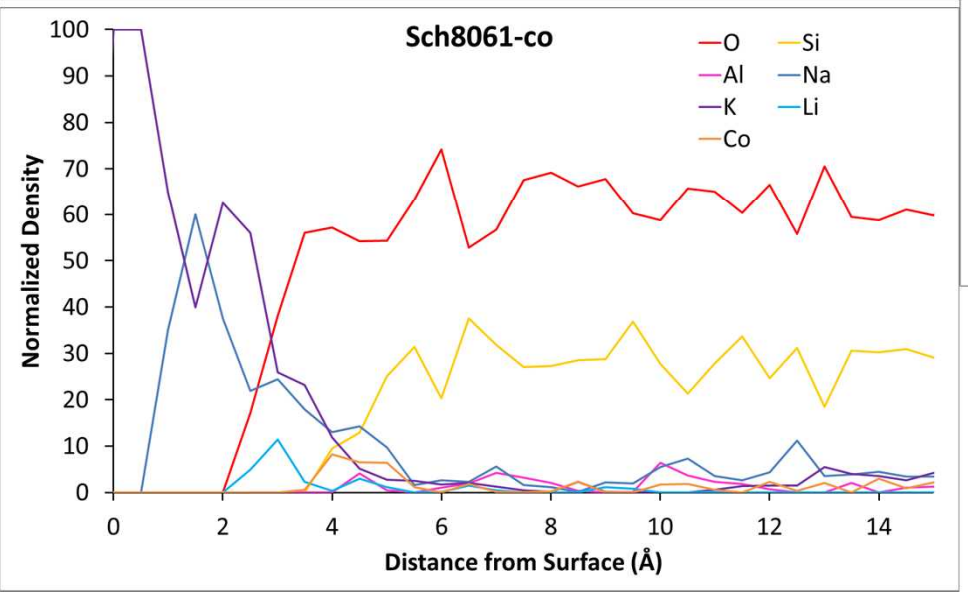
MD Simulations Show That
Glass Modifiers Migrate To The Surface Of the Glass

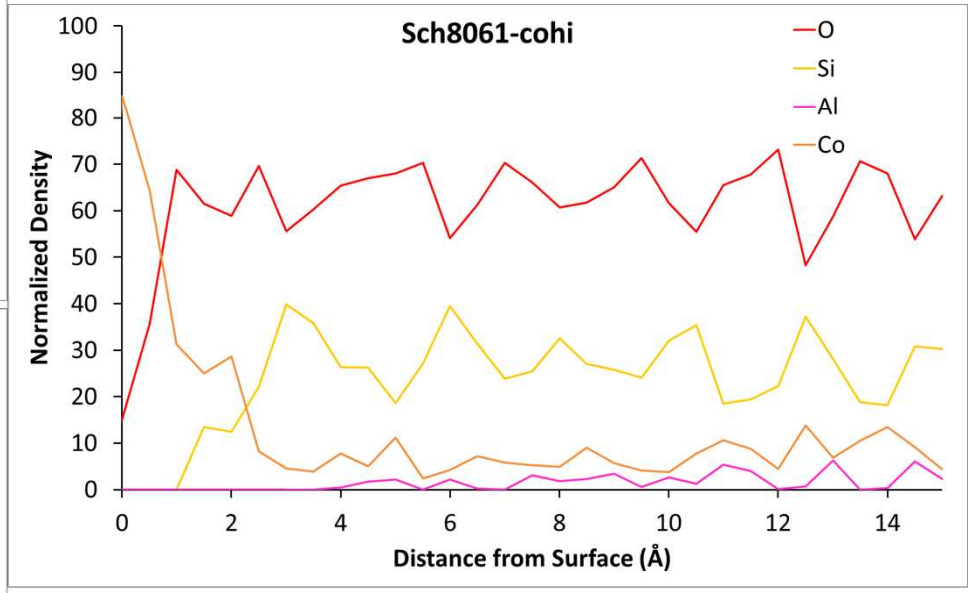




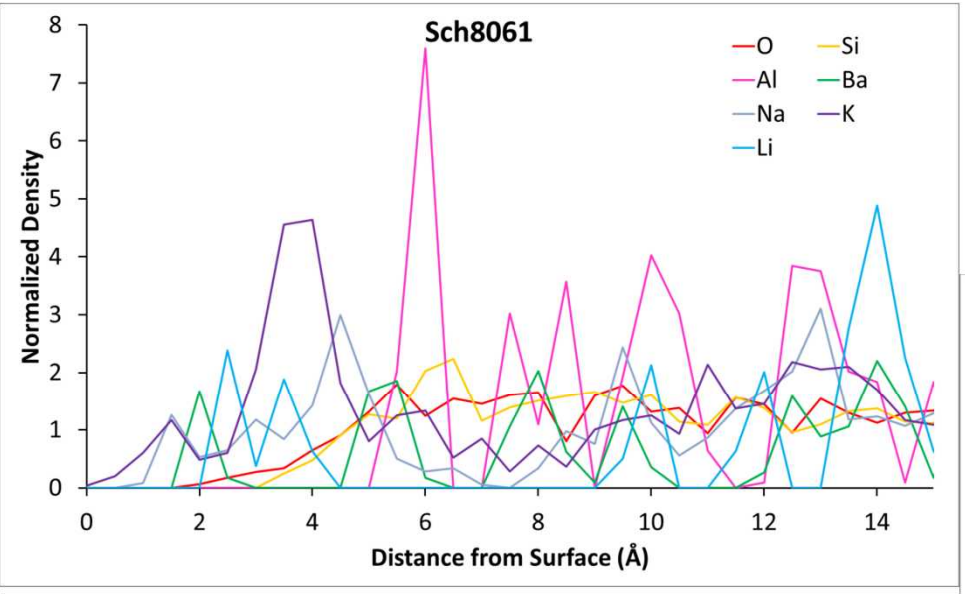
Surface density profiles (normalized by total density in each bin—normalized density adds to 100% in each bin); single surface

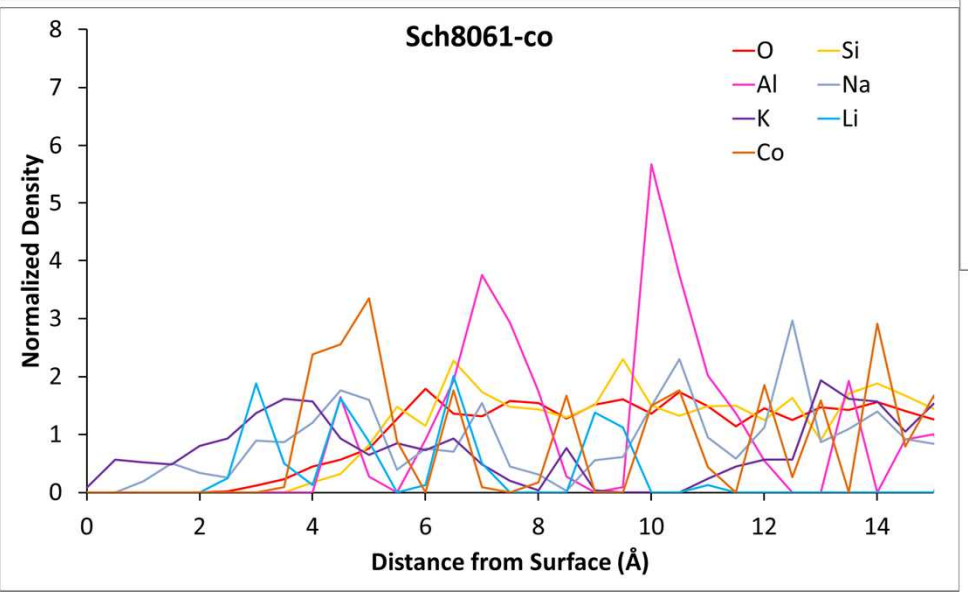


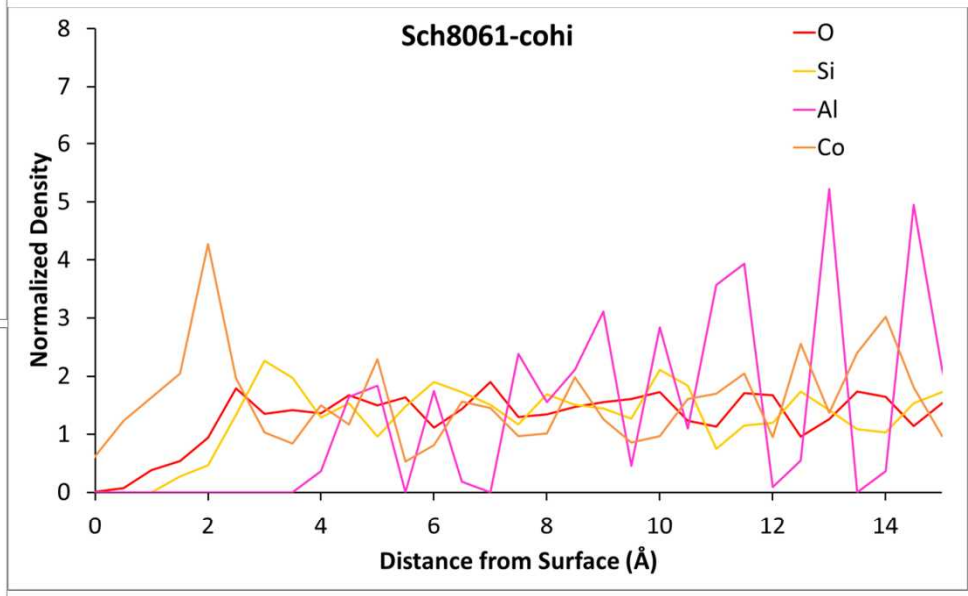




Surface density profiles (each curve normalized by total number of atoms of that type in the simulation); single surface







Creating multiple surfaces from different cuts to the original bulk structure will help to smooth out the curves.

Experimentally-Validated Glass Structure & Property Modeling Is Being Developed To Enable Advanced FGC Design

- **Conclusions**
  - Glass Structure & Properties Can Be Modeled With MD Code and the Pedone FF
    - Good first-order agreement between experiment & model structures
    - Good agreement between experiment & model densities
    - Modeling is an efficient means to assess chemistry-structure relations
  - There is Room for Improvement in Modeling & Experiment
    - Differences between modeling and experiment suggest room to improve potentials
    - Property predictions are challenging, and may be limited to predicting trends
    - Modeling low concentration constituents in the bulk is not practical
    - Modeling Interface segregation may be a practical approach for surface active elements
    - Enhanced experimental technique & analysis are needed to test/validate modeling
- **Future Work**
  - Refine Experiments/Analyses
    - Higher resolution experiments
  - Advance Glass Modeling
    - Extend modeling to glass interfaces
  - FGC Composite Processing & Characterization