Characterization & Modeling of Glass Chemistry-Structure-Property Relations To Develop Advanced Glass Composite Joining Materials

ICACC-S8-045-2015

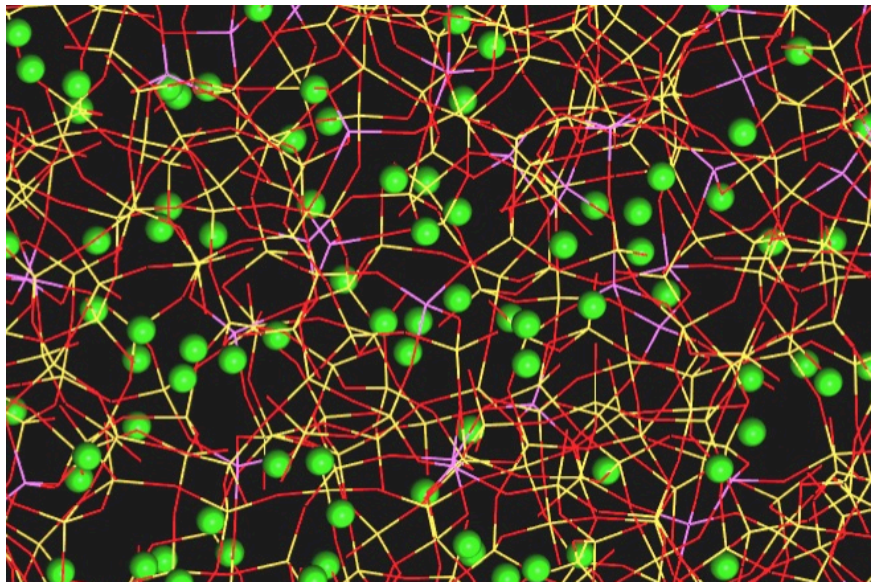
Kevin G. Ewsuk, Todd R. Zeitler,
Michael T. Brumbach, Mark A. Rodriguez,
Todd M. Alam, & Louise J. Criscenti
Sandia National Laboratories
Albuquerque, NM 87185

39th International Conference & Exposition on Advanced Ceramics & Composites
Daytona Beach, FL
January 29, 2015

SAND2015-0368C

Exceptional service in the national interest

Sandia National Laboratories



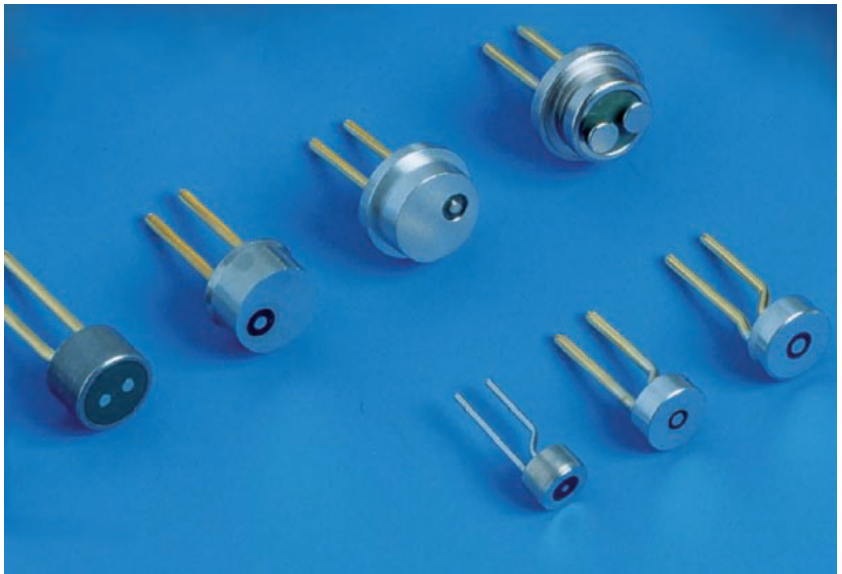
25 BaO - 5 Al_2O_3 - 70SiO_2 Glass

Symposium: S8:
9th International Symposium on Advanced Processing and Manufacturing Technologies for Structural and Multifunctional Materials and Systems (APMT9)

Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.
SAND No. 2011–XXXXP.

Glass Is Used To Bond Or Join Materials

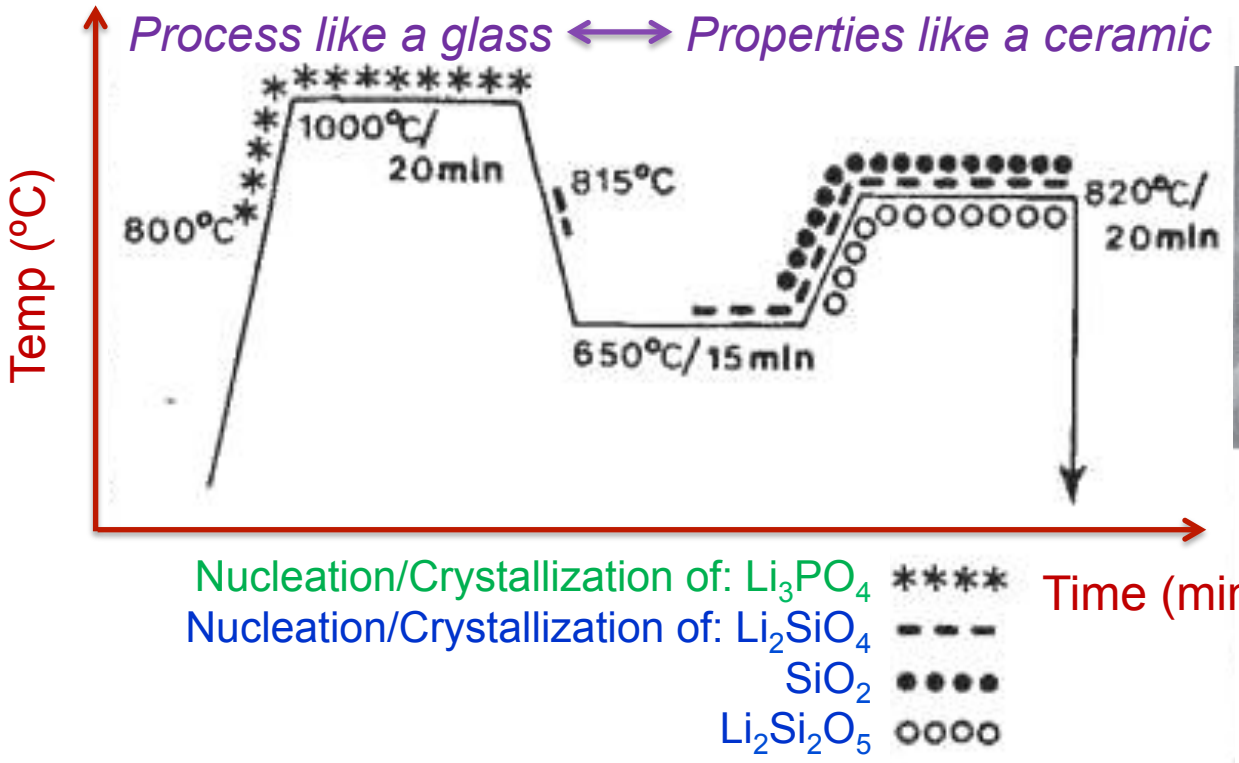
- **Glass bonding/joining Applications**
  - Glass bonded composites
    - Glass-bonded alumina
    - Low temperature co-fired ceramic LTCC electronic packaging
  - Glass to metal (GtM) Seals
    - Hermetic electrical feed-troughs
- **Glass Attributes for GtM Sealing**
  - Processability
  - Materials Compatibility
  - Durability
- **Glass Deficiencies for GtM Sealing**
  - Properties
    - Low CTE
    - low toughness/crack tolerance
  - Reactivity & Stability
- **Alternatives to Glass for GtM Sealing**
  - Glass-Ceramics
  - Filled-Glass Composites (FGCs)

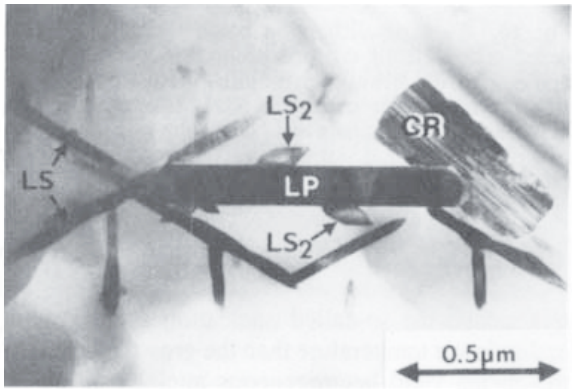


Glass-Ceramics Offer Higher CTEs & Ceramic-Like Properties At The Expense Of Processability

Sandia National Laboratories

Thermal Processing Determines The Microstructure & Properties Of The Glass-Ceramic

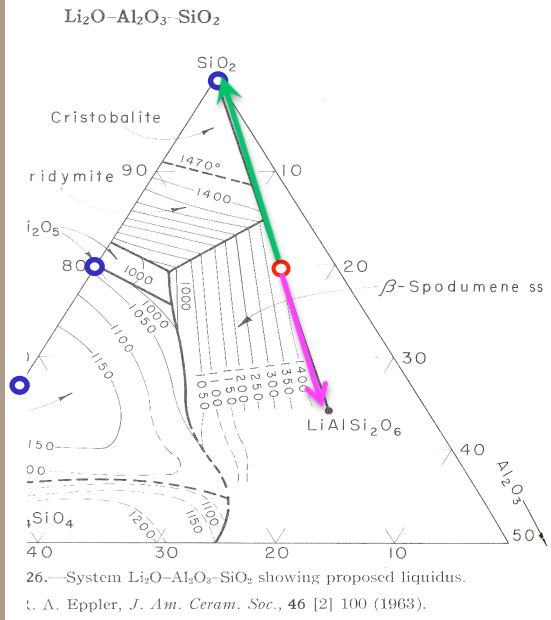




Headley & Loehman, "Crystallization of a Glass-Ceramic by Epitaxial Growth", J Am Ceram Soc, 67 [9] 620-25 (1984).

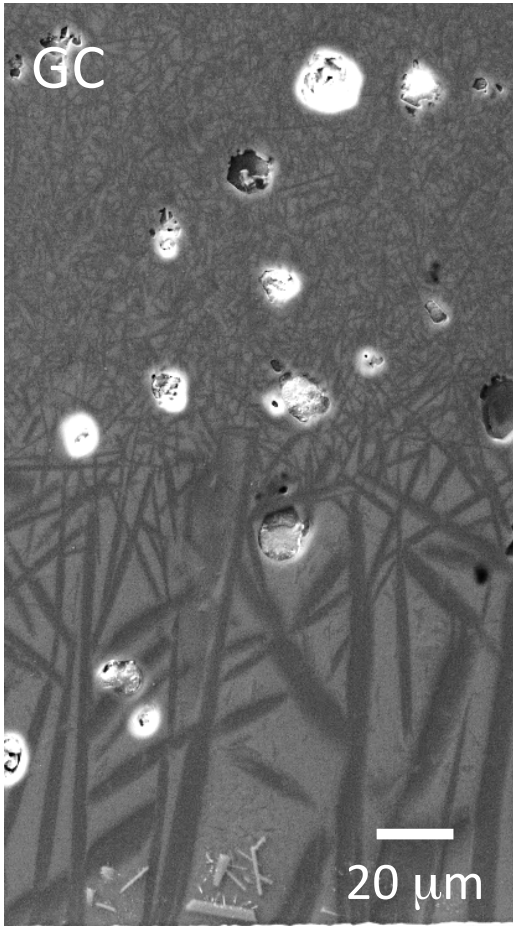
A Glass-Ceramic Seal/Interface Is Affected By Glass-Metal Interdiffusion & Glass Devitrification

Sandia National Laboratories



26.—System Li_2O–Al_2O_3–SiO_2 showing proposed liquidus.

t. A. Eppler, *J. Am. Ceram. Soc.*, **46** [2] 100 (1963).



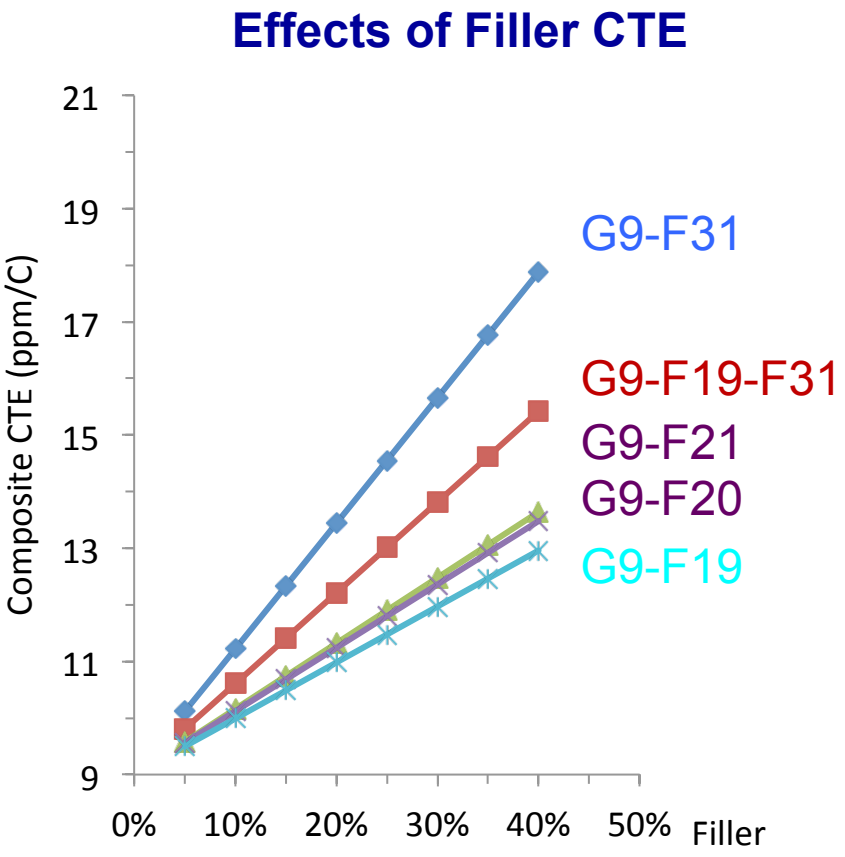
Glass-Ceramic

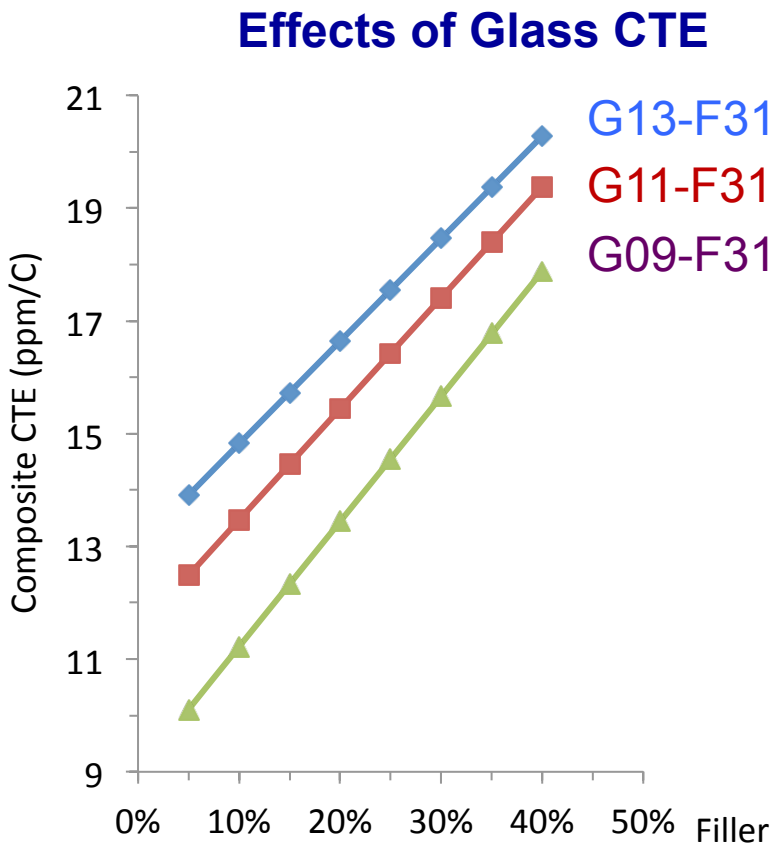
Rxn Zone

Stainless Steel

A Filled-Glass Composite Combines The Attributes Of A Glass (Processability) And A Ceramic (Properties)

Sandia National Laboratories





- Glass processability & ceramic properties
- High/Tailorable CTE
- Microstructural Stability

The Goal Is to Develop Improved Performance & Reliability Bonding Glasses

Sandia National Laboratories

- **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 model 3-component glass,
    - In more complex glasses
    - At interfaces
  - Compare/contrast modeling & experimental results
- **Future Work**
  - Test, refine, & validate modeling/simulation by comparison to experiment.
  - Design/Fabricate Filled-Glass Composites

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

Sandia National Laboratories

	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.

25 BaO - x Al_2O_3 - y B_2O_3 (75 - x - y) SiO_2 Glasses Were Melted & Characterized

Sandia National Laboratories

Glass	Oxide Mole %				g/ mole	Mole% Al_2O_3 + B_2O_3	Archimedes Density (g/cc)	He Pycnometer Density (g/cc)	Measured T_g (°C)	Measured C_p (J/g K) @35 °C
	BaO	Al_2O_3	B_2O_3	SiO_2						
BAS 8	33	0	0	66.6	91.1	0		3.69		0.636
BAS 1	25	0	0	75	83.4	0	*3.52	*3.33	---	---
BAS 2	25	5	0	70	85.5	5	3.25	3.31	780	0.635
BAS 3	25	15	0	60	89.7	15	3.22	3.31	751	0.619
BABS 5	25	23	6	46	93.6	29		3.27	609	0.724
BABS 6	25	21	12	42	93.3	33		3.25	611	0.666
BABS 7	25	19	18	38	93.1	37		3.22	607	0.679

- BAS glass 1, 2, 3 were also simulated

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

Sandia National Laboratories

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

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

- Simulations with more atoms are slightly improved
- Density determines box size, which affects results
- Simulation parameter sensitivity studies will be completed

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).*

Pedone Potentials Are Available To Model More Complex Glass Compositions

Sandia National Laboratories

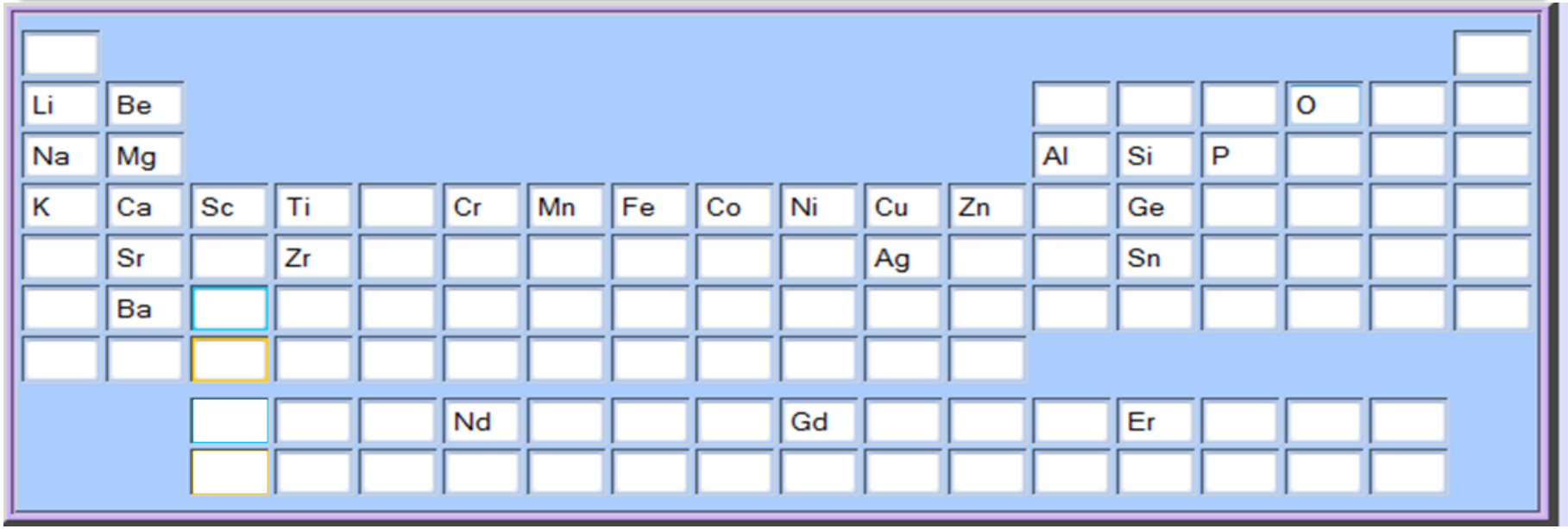


TABLE 2: Potential Parameters of Eq 4 Derived from Binary Oxides[a]

	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]

More Complex Glasses Have Been Simulated And Are Being Analyzed

Sandia National Laboratories

	SiO_2	Al_2O_3	BaO	CaO	B_2O_3	Na_2O	K_2O	density (g/cm^3)
BAS1	75		25					3.294
BAS2	70	5	25					3.314
BAS3	60	15	25					3.330
BAS8	66.7		33.3					3.685
CAS1	75			25				2.512
CAS2	70	5		25				2.544
CAS3	60	15		25				2.586
CAS8	66.7			33.3				2.626
TRZ01	55	20	25					3.318
TRZ02	50	25	25					3.307
Cor9013Na	70	3.5	12			14.5		2.892
Cor9013K	70	3.5	12				14.5	2.860
PC1	50		10			40		2.990
PC2	50		30			20		3.762
TRZ03	50		20			30		3.393
TRZ04	50		10			10	30	2.907
TRZ05	50		10			20	20	2.932
TRZ06	50		10			30	10	2.959
TRZ07	50	10	10				30	2.897
TRZ11	50	10	10			30		2.968

← from SciGlass

Original BAS runs

Original - substituting CaO for BaO

Supplement original - higher Al_2O_3

Modified original - alkali for Al_2O_3

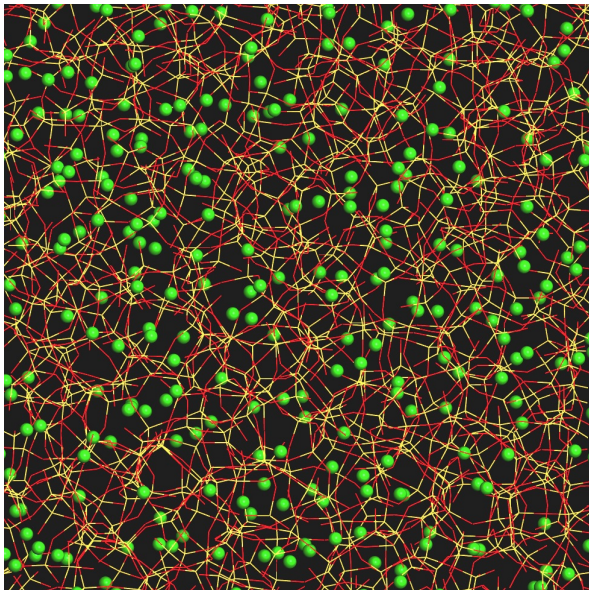
Modified original - w/alkali & Al_2O_3

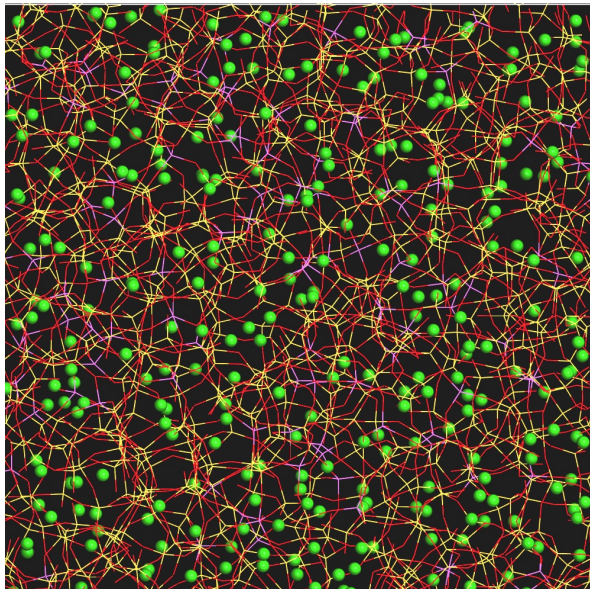
BAS Glasses Were Simulated With The LAMMPS** MD Code & Pedone* Multicomponent Force Field

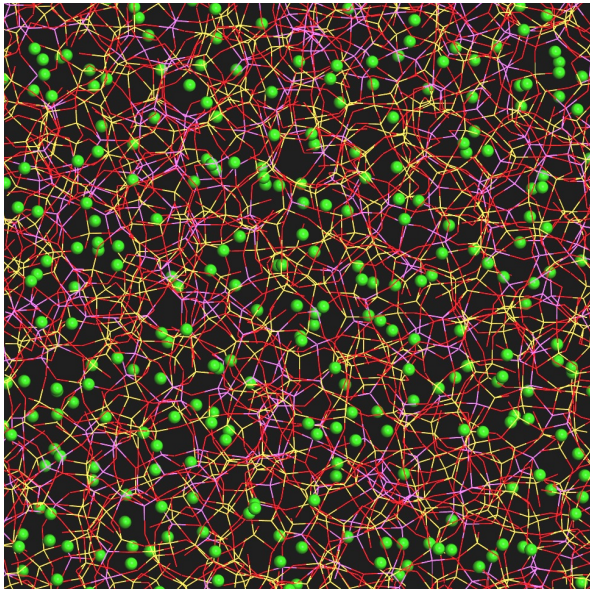
Sandia National Laboratories

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

BAS 1	BAS 2	BAS 3
25BaO-75SiO_2	25BaO-5Al_2O_3-70SiO_2	25BaO-15Al_2O_3-60SiO_2







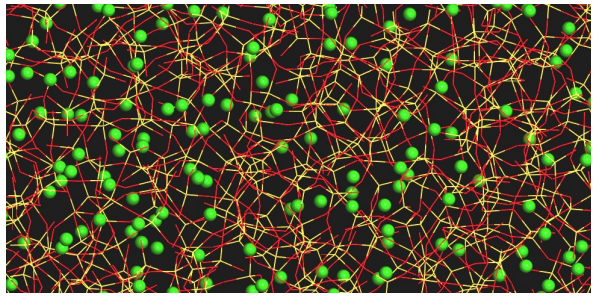
A Pedone et al., "A new self-consistent empirical interatomic potential model for oxides, silicates, and silica-based glasses", J Phys Chem B, **110, 11780-11795 (2006).*

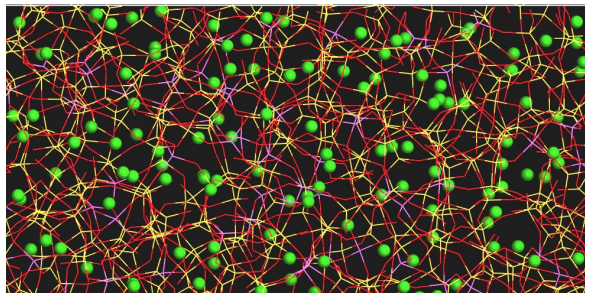
***S Plimpton, "Fast Parallel Algorithms for Short-Range Molecular-Dynamics, J Comp Phys, **117** [1], 1-19 (1995).*

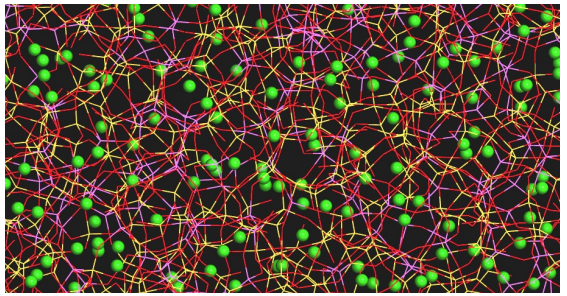
The Simulated BAS Glasses Were Analyze Using Cormack Post Processing Tools

Sandia National Laboratories

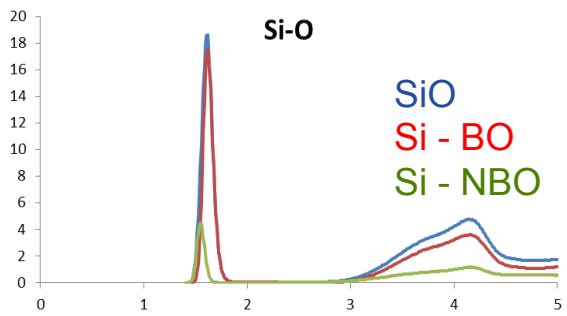
BAS 1	BAS 2	BAS 3
$25BaO\text{-}75SiO_2$	$25BaO\text{-}5Al_2O_3\text{-}70SiO_2$	$25BaO\text{-}15Al_2O_3\text{-}60SiO_2$

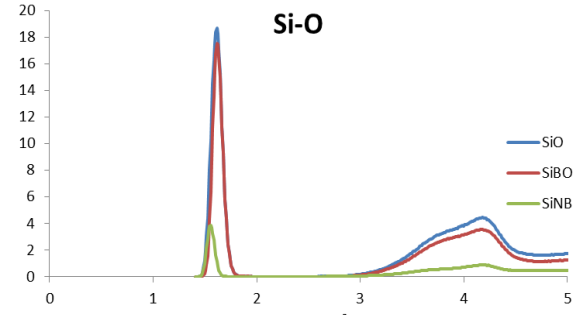


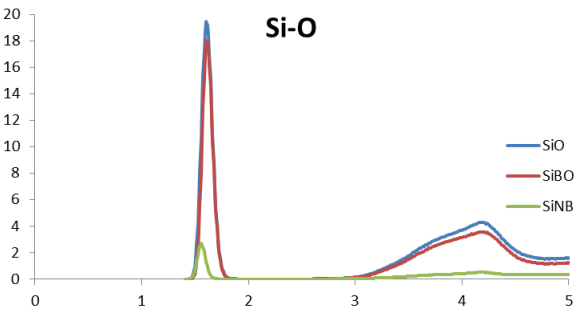




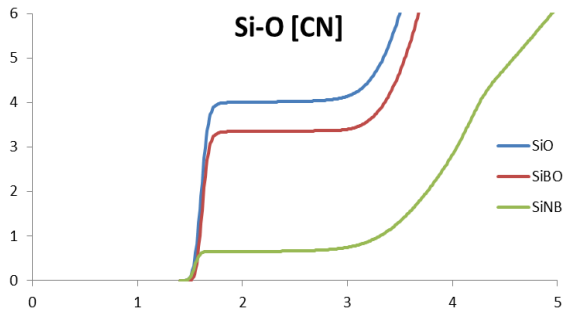
Pair Dist. Function

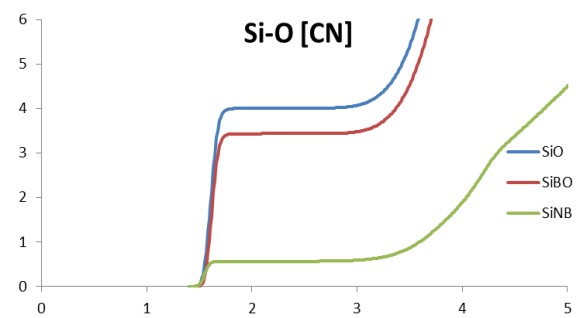


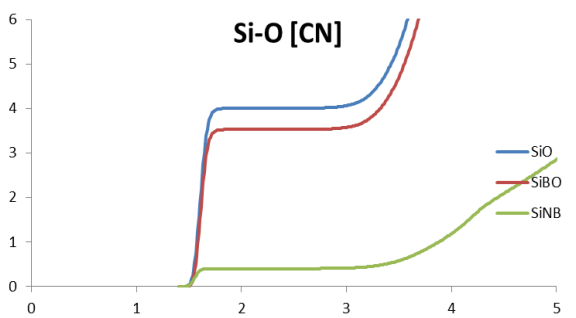




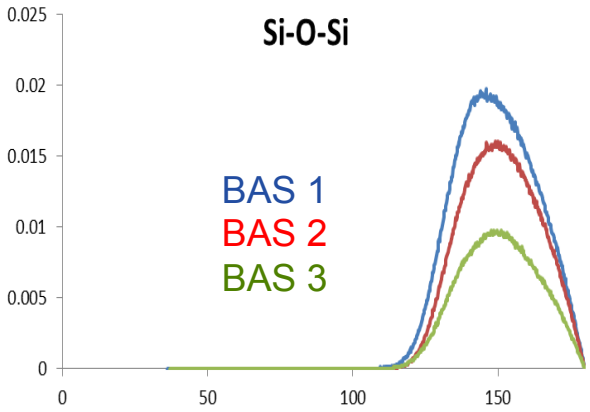
CN





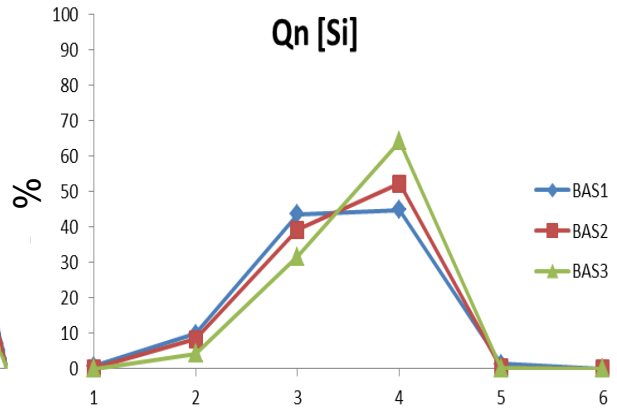


Chemistry-Structure Relationships Were Analyzed In The Simulated BAS Glasses



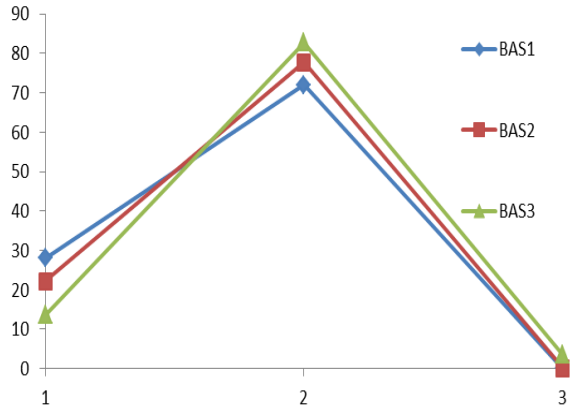
Bond Angle (Å)

Peak position & symmetry increase from BAS1→ BAS2→BAS3 related to short to mid-range order



n

Q4/Q3 (CN) increases from BAS1→BAS2→BAS3 with decreasing non-bridging oxygen ions (NBO)

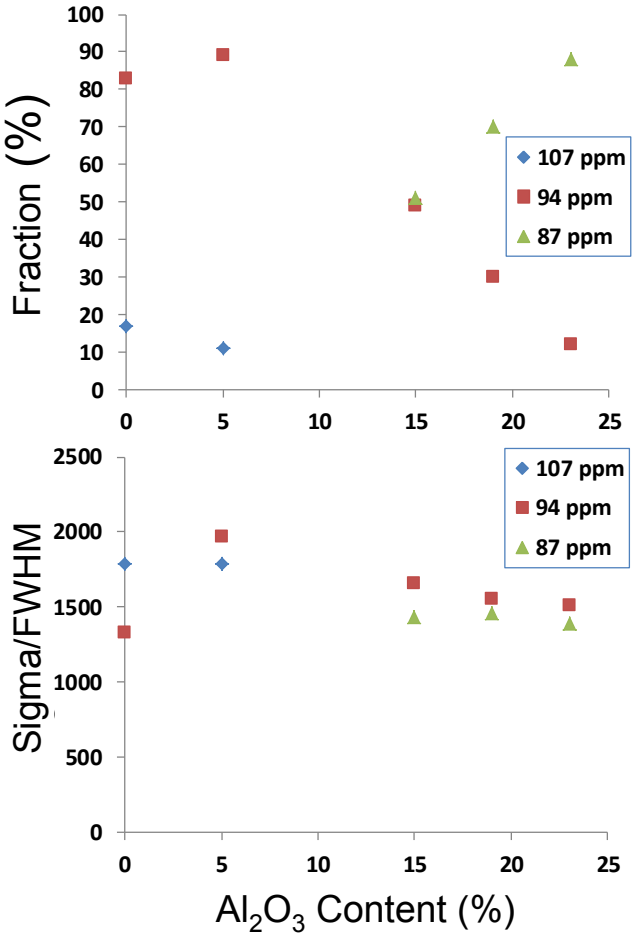


Oxygen Speciation
1 = BO, 2 = NBO, 3 = TBO

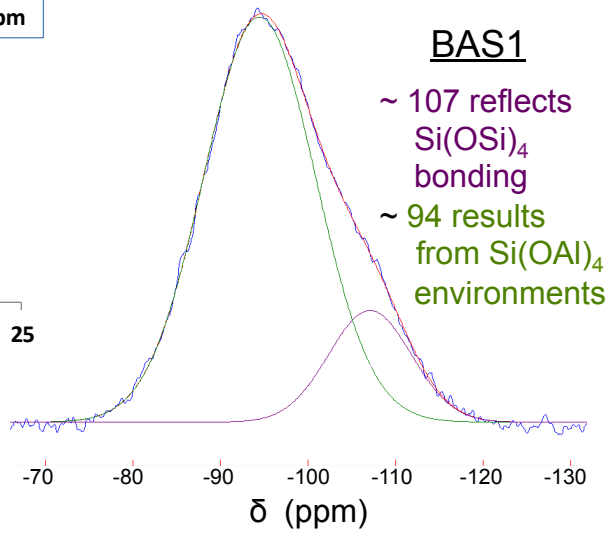
The ratio of bridging oxygen ions (BO) to NBOs increases from BAS1→BAS2→BAS3

Bonding/Structure Were Characterized Using Nuclear Magnetic Resonance (^{27}Al & ^{29}Si NMR)

Sandia National Laboratories



Sample	δ (ppm)	FWHM (Hz)	Fraction(%)
BAS-1	-107.1 -94.5	1792 1326	17 83
BAS-2	-107.1 -94.7	1792 1971	11 89
BAS-3	-107 -94.7 -87.9	-- 1658 1430	0 49 51
BAS-5	-107 -94.7 -87.4	-- 1509 1389	0 12 88
BAS-7	-107 -94.7 -87.9	-- 1552 1457	0 30 70

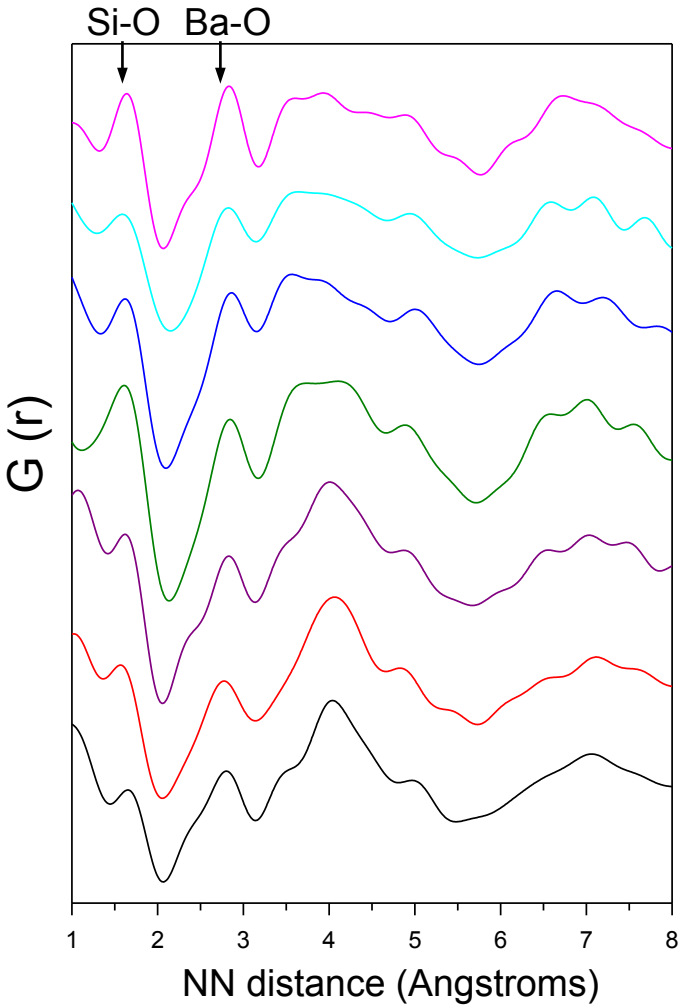


^{29}Si MAS NMR Spectra

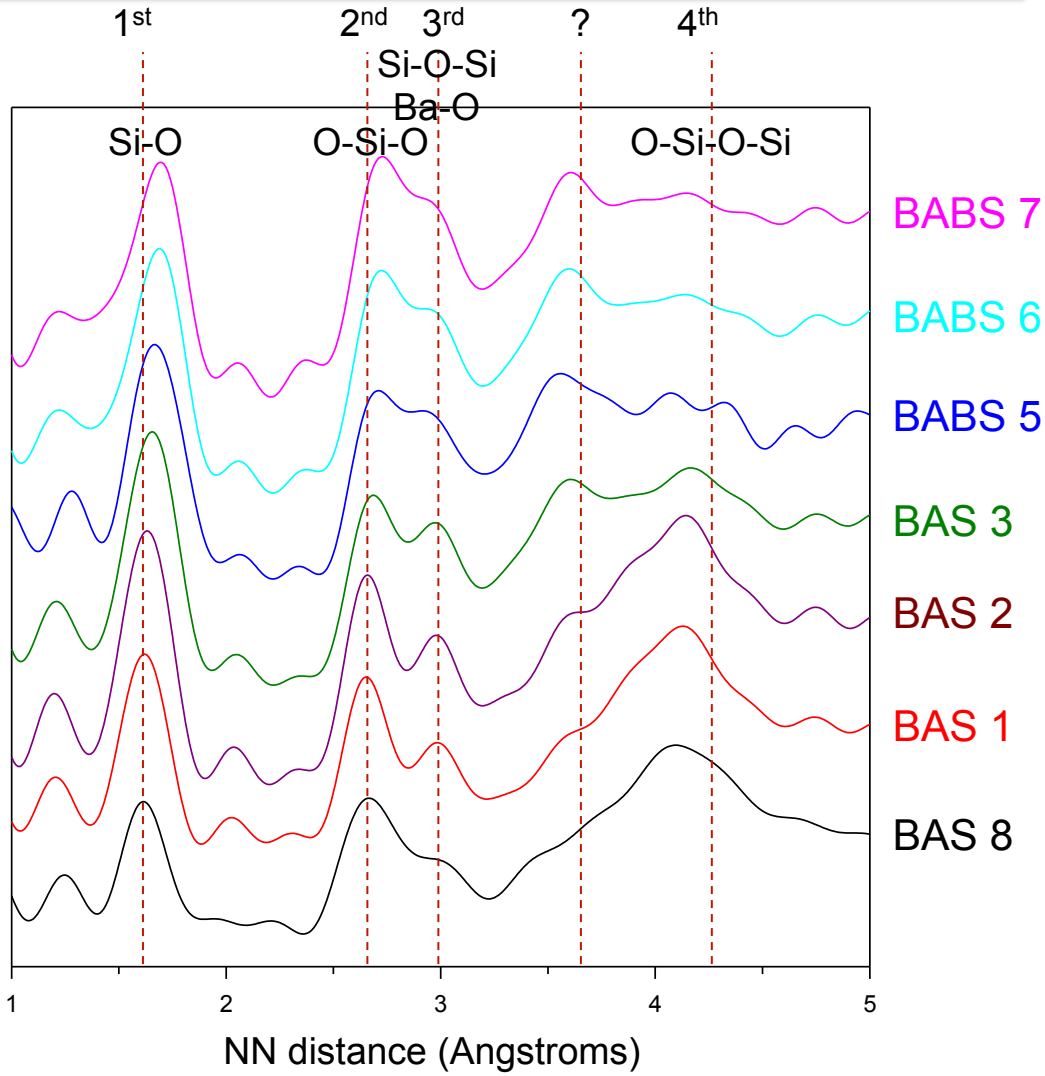
- The chemical shift reflects changes in the Si-O bond length & local modifier concentrations.
- The peak/line width (FWHM) reflects local disorder.

Atomic Pair Distribution Functions (aPDFs) Were Used To Assess Chemistry-Structure Relationships

Sandia National Laboratories



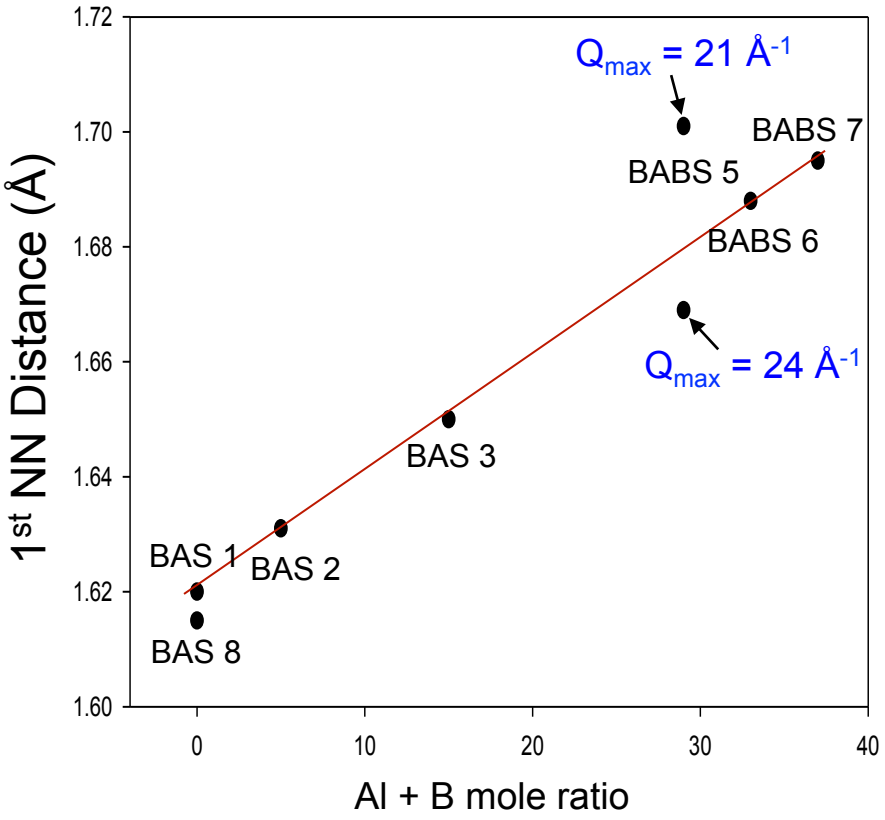
Lab-based aPDF analysis
(λ = 0.7017 Å; Q_{max} = 12 Å^{-1})



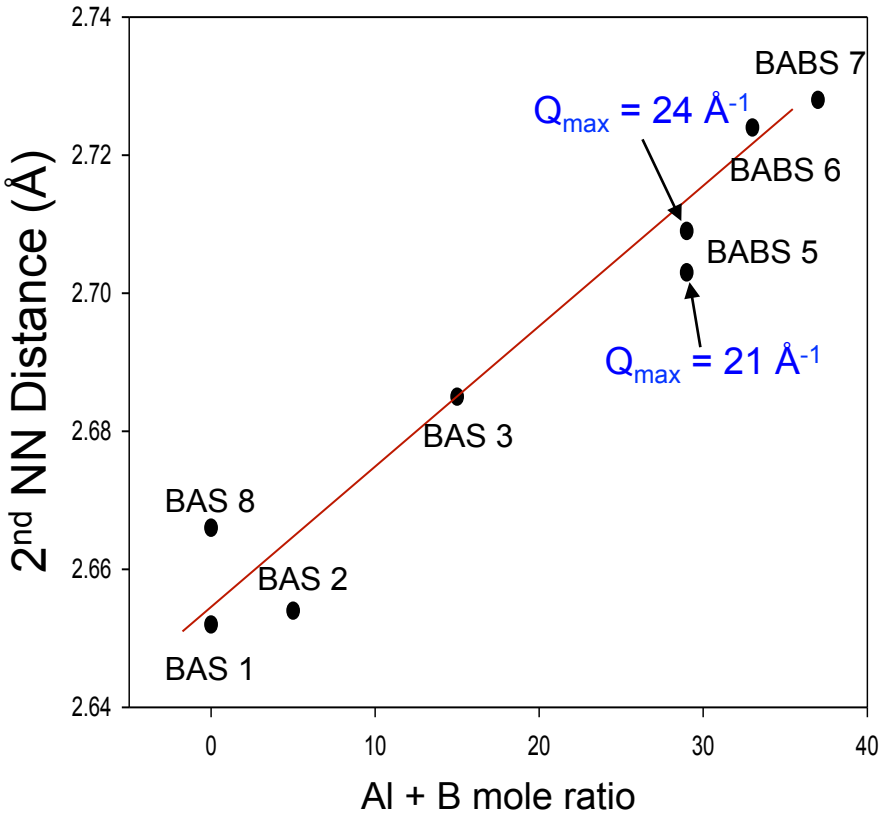
Synchrotron-based aPDF analysis
(λ = 0.1430 Å; Q_{max} = 21 Å^{-1}).

The 1st & 2nd Nearest Neighbor (NN) Distances In The BAS Glass Structure Are Related To The Si-O Tetrahedron

Sandia National Laboratories

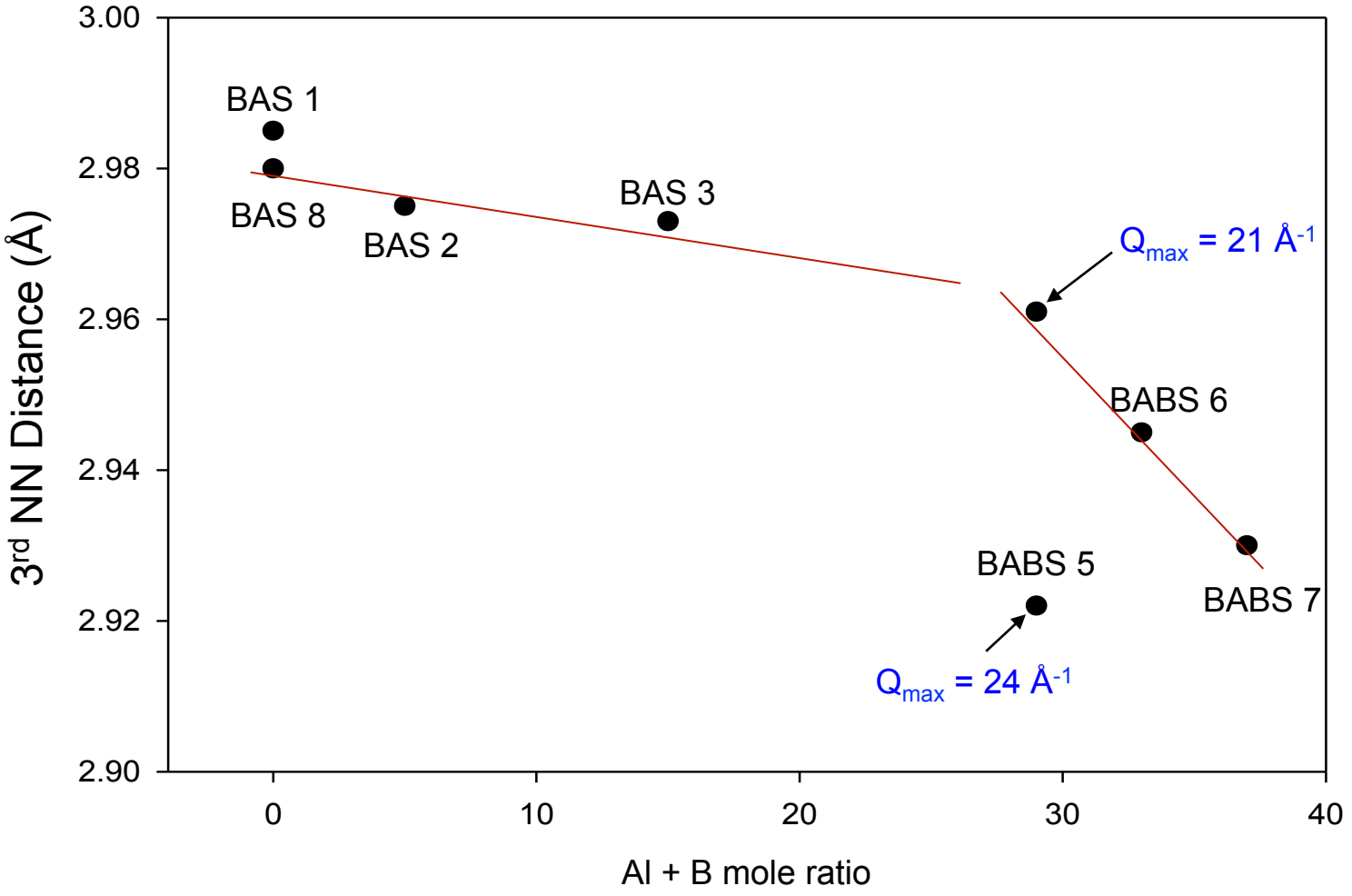


~+0.002 Å increase in Si-O Bond length for every mole % addition of Al+B.



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

The 3rd NN Distance May Be A Convolution Of The Ba-O Average Bond Length & The Si-O-Si Distance



The average distance between Si atoms that reside in different SiO_4 tetrahedrons and are linked by a bridging oxygen (BO).

Comparisons to Experiment Are Being Used To Test, Refine, & Validate Model Predictions

Sandia National Laboratories

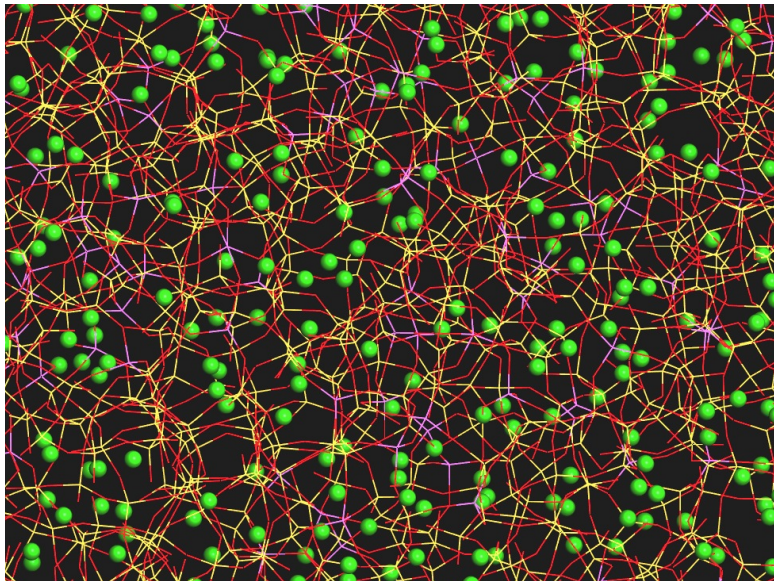
Tool	Bond Lengths	Bond Assignments	Coordination Number	Comments	Glasses
Model	Y	Y	Y	Bond Angle Distributions, BO's/ NBO's	BAS 1-3,8
aPDF	Y	inferred			BAS 1-3,8 BABS 5-7
NMR	Trends			Order/Disorder Trends	BAS 1-3,8 BABS 5-7

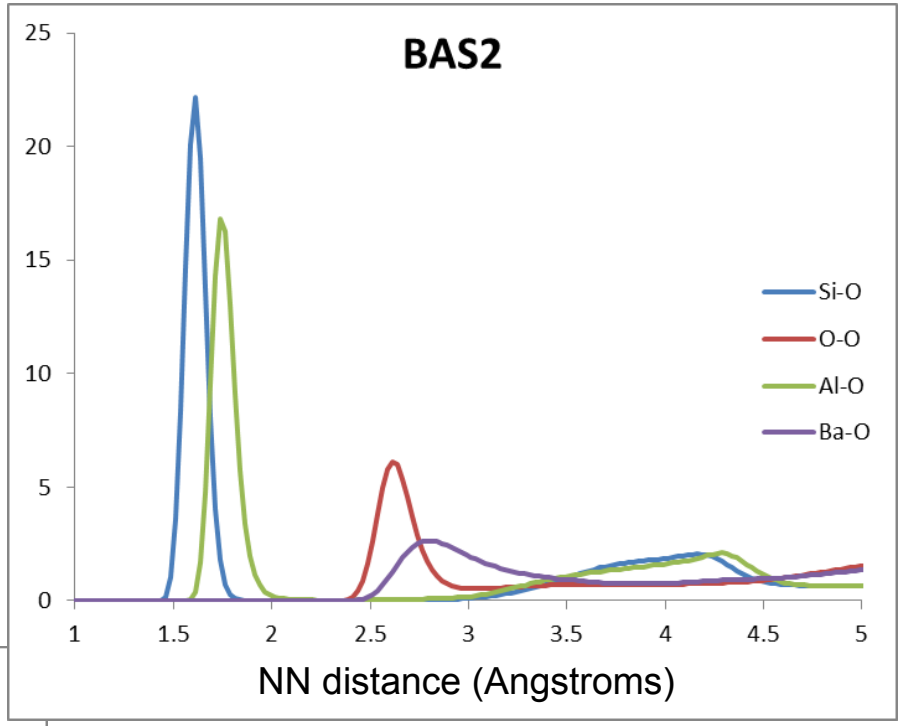
- EXAFS will provide Ba coordination information

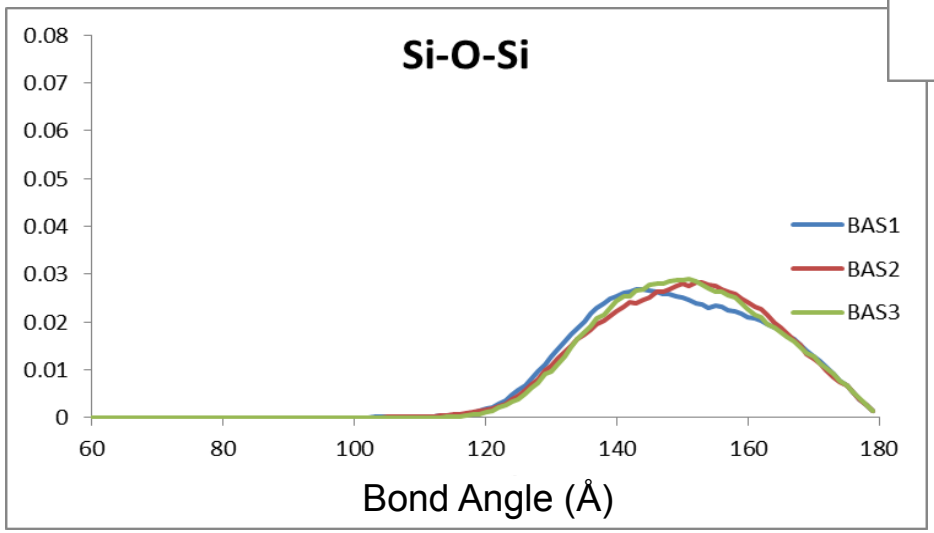
Modeling & Post Processing Were Completed On 25 BaO - x Al_2O_3 - (75 - x) SiO_2 Glasses

Sandia National Laboratories

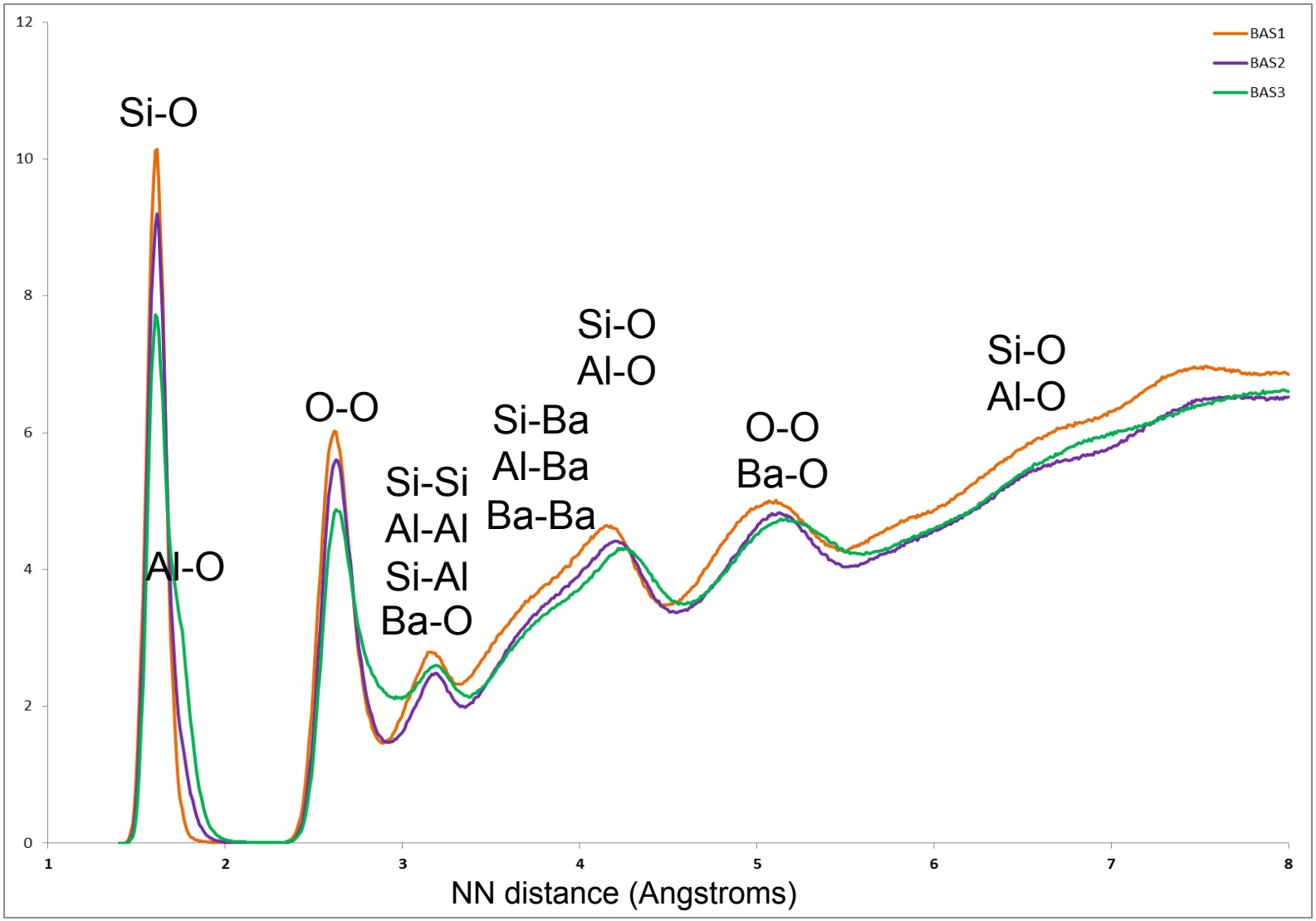
25 BaO - 5 Al_2O_3 – 70 SiO_2







Model Peak Assignments Are Consistent With aPDF Peak Assignments



Refinements In Modeling & Experiment Are Required To Understand Glass Chemistry-Structure Relations

Sandia National Laboratories

	Model	XRD	NMR
1st NN	Si-O length independent of Al	Si-O (+ Al-O) length increases w/ Al	No ^{29}Si peak shifts or peak with changes
2nd NN	O-O length increases w/Al	O-Si-O length increases w/Al	
3rd NN	Ba-O length higher w/Al	Ba-O length increases w/Al	
4th NN	Ba-Ba length increases w/Al	Peak assignment unclear	

Possible Refinements

- Higher resolution equipment
- Modified analysis of results
- Tweaking interatomic potentials

Model & Experimentally Determined BAS Glass Physical Properties Are Being Compared/Contrasted

Sandia National Laboratories

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)
BAS8	91.1	0					3.69	3.69 ± 0.01
BAS1	83.4	0	28.6	28.0	1.7	3.29	3.32	3.31 ± 0.01
BAS2	85.5	5	22.2	22.1	1.8	3.31	3.31	3.32 ± 0.02
BAS3	89.7	15	10.5	13.6	1.9	3.33	3.31	3.39 ± 0.01

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)
BAS8	---	---	0.636				
BAS1	---	1473 ± 95	---	0.858 ± 0.004		11.6 ± 0.5	31.0 ± 6.3
BAS2	780	1365 ± 225	0.635	0.867 ± 0.004		10.4 ± 0.6	24.1 ± 6.1
BAS3	751	1394 ± 116	0.619	0.884 ± 0.004		10.1 ± 0.4	19.1 ± 4.2

- Modeling glass physical properties is challenging

Summary

- **Work Completed**
  - Melted BaO-Al_2O_3-SiO_2 (BAS) & BaO-Al_2O_3-B_2O_3-SiO_2 (BABS) glasses.
  - Adapted/Applied Pedone interatomic potentials in LAMMPS MD code and simulated BAS glass.
  - Applied Cormack post processing tools to analyze glass structure & properties
  - Characterized BAS and BABS glass chemistry (XPS), structure (XAFS, NMR, & aPDF) & physical properties.
  - Comparing results from modeling & experiment.

- **Future Work**
  - Refine Experiments/Analyses
  - Advance Glass Modeling
    - Test & refine model predictions by comparison to experiment.
    - Model/analyze more complex glasses & glass interfaces.
    - Develop/apply capability to model B.
    - Extend modeling from bulk glass to glass interfaces.