SAND2016-6000C

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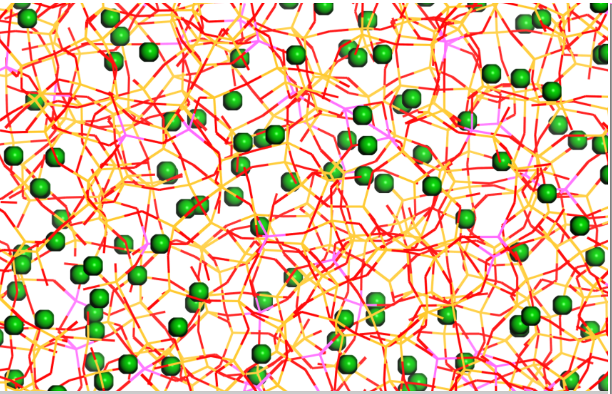
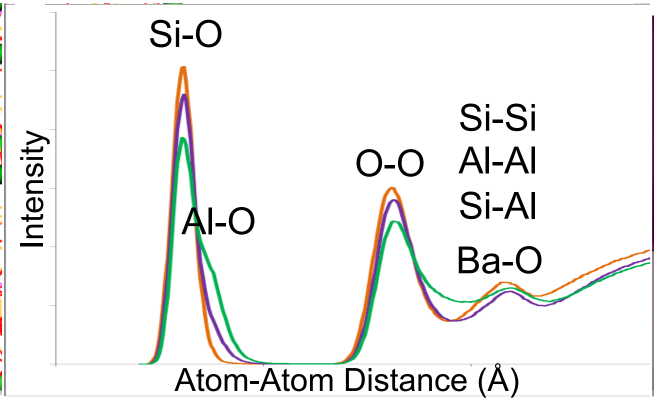
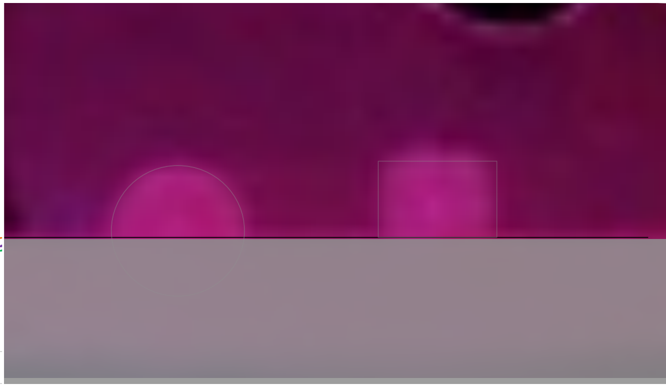
LDRD

2:30–3:00 Trinity III

G1 - Powder processing innovation and technologies for advanced materials and sustainable development







Characterization and Modeling to Design and Develop Particle-Filled Glass Composites

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

9th International Conference on High Temperature Ceramic Matrix Composites (HTCMC-9) and Global Forum on Advanced Materials and Technologies for Sustainable Development (GFMAT 2016)

June 26 – July 1, 2016

Toronto, Ontario, Canada

U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

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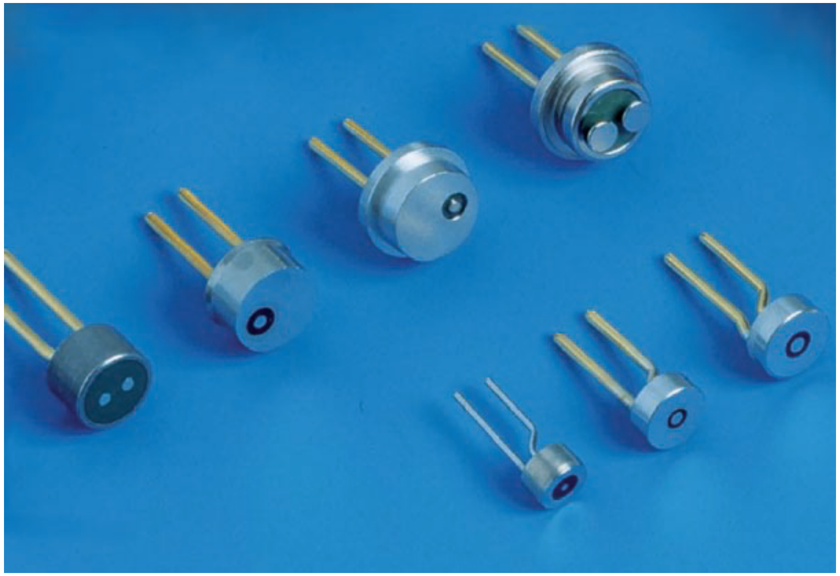
Glass Is Commonly Used To Bond/Join Inorganic Materials

- **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 bag igniters
      - Medical implants
      - Microelectronics
    - Energy conversion
      - Solid oxide fuel cells (SOFCs)
      - Concentrated solar

*Feedthroughs for pressure & flow sensors



*Airbag igniter feedthroughs

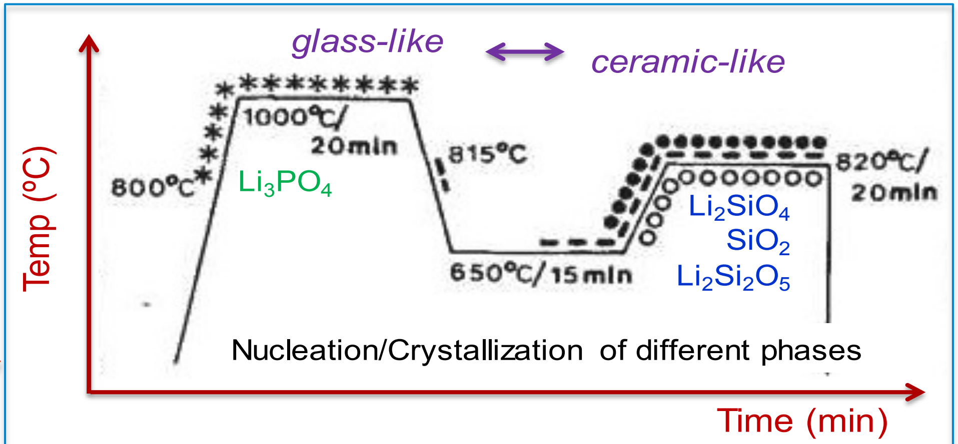
*Schott Electronic Packaging

Glass Ceramics Offer Enhanced Performance At the Expense of Processability

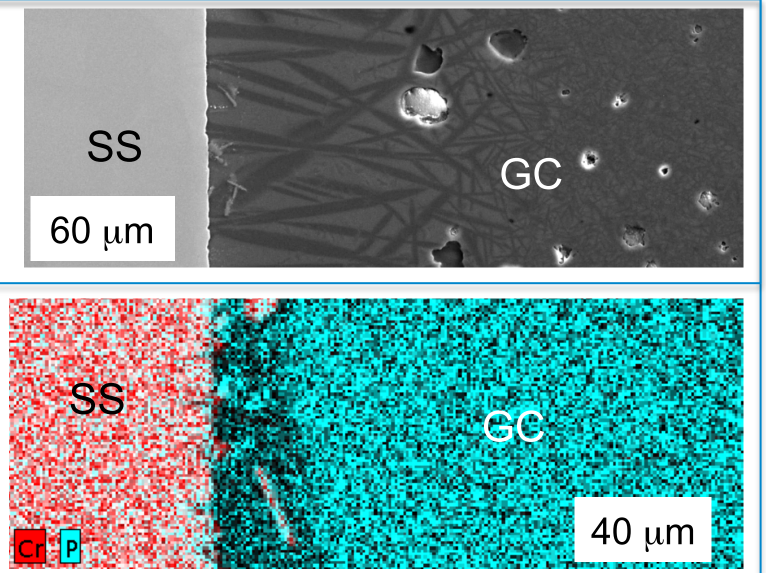
Glass
- + Processability
- + Materials Compatibility
- - Low/fixed CTE
- - Low toughness/crack tolerance

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).



Residual GC Glass Chemistry & Properties Change With Silicate Crystallization

Crystal Product	Glass SiO_2 Content	Glass Viscosity
Silicates	↓	↓

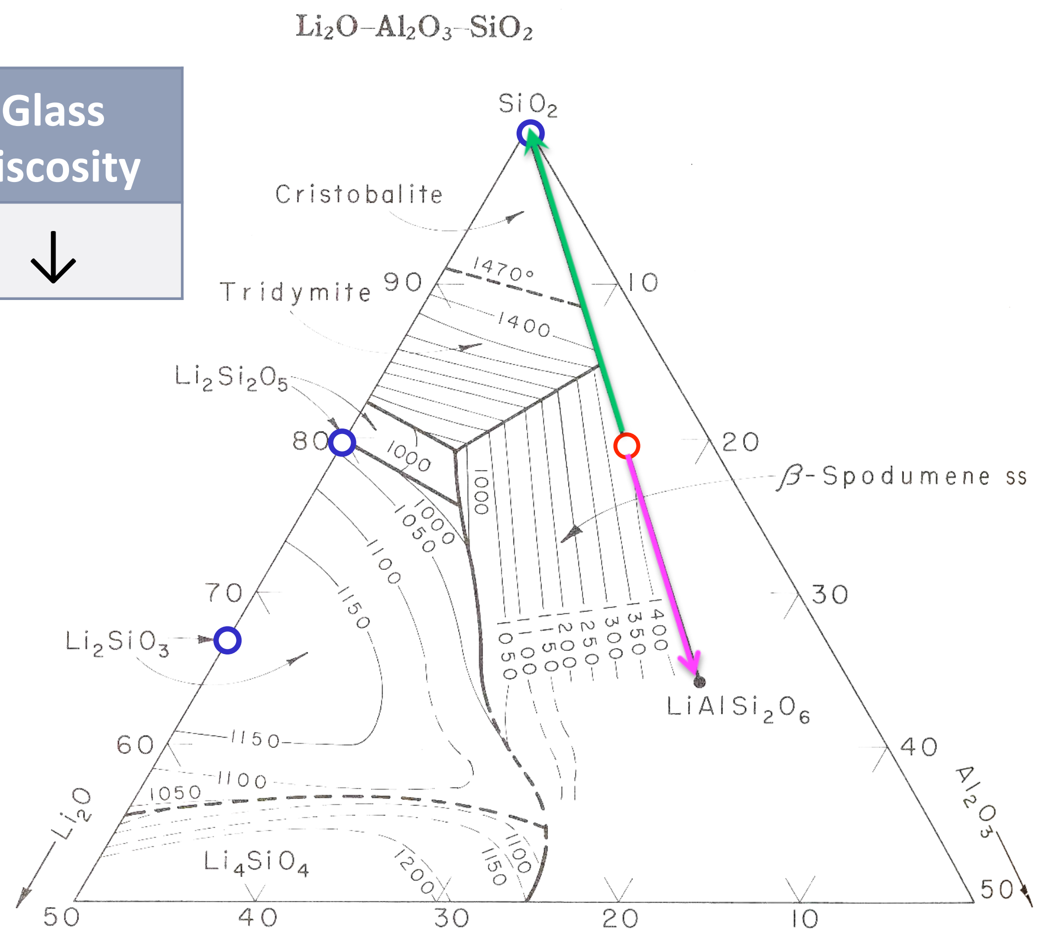


FIG. 2426.—System Li_2O–Al_2O_3–SiO_2 showing proposed liquidus.

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

FGCs Combine The Performance Of A Glass-Ceramic With The Processability Of A Glass

	Glass	Glass-Ceramic (GC)	Filled Glass Composite (FGC)
Microstructure	amorphous	crystalline ceramic in glass matrix	ceramic and/or metal particles in glass matrix
Applications	matched & compression seals	low to high CTE matched & compression seals	low to high CTE matched & compression seals; graded seals
Seal Issues	glass cracking & chipping	hermeticity	---
Processing	glass flows freely to seal	glass softens/flows freely to seal; devitrifies to GC	glass softens with limited flow in FGC to seal
Manufacturability	robust/simple/forgiving	t-T process sensitive microstructure/properties	robust/simple/forgiving;
Process Sensitivity	low	high	low
CTE	low; ~ linear	tunable	tunable
Attributes	Processability & proven history	performance	processability & performance & reliability & engineered properties
Deficiencies	low strength & toughness	different interface chemistry, microstructure, & properties	systems need to be designed/ developed

Characterization & Modeling Are Being Employed To Design/Develop Advanced Filled-Glass Composites (FGCs)

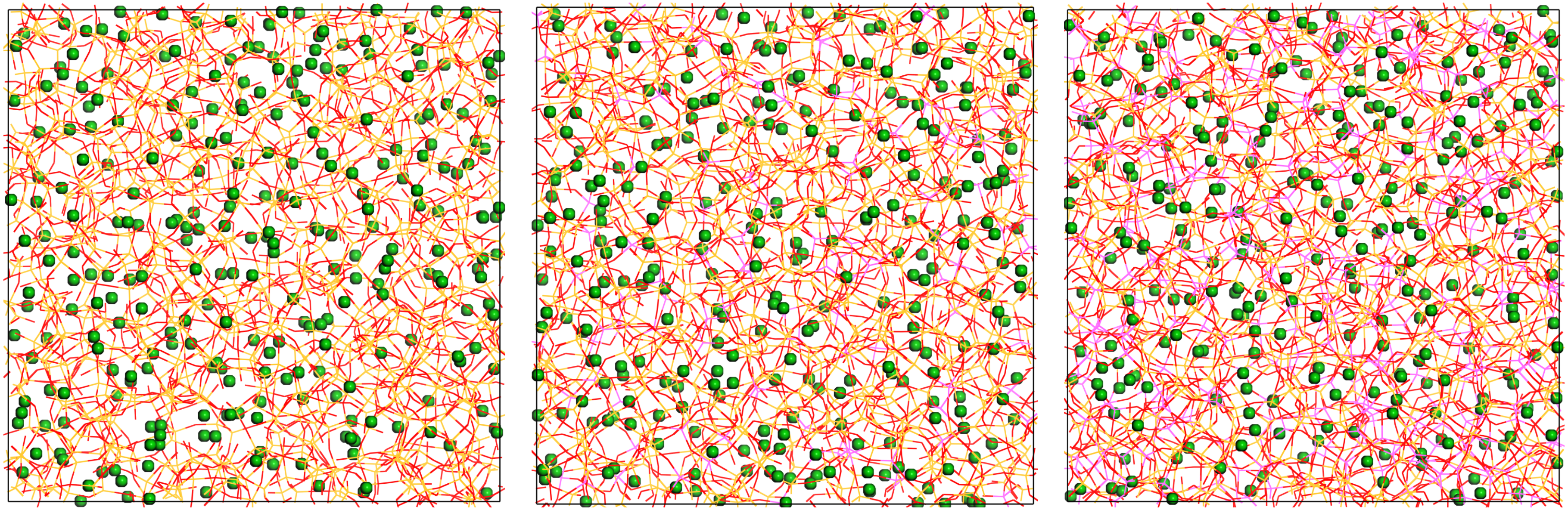
- **Objectives**
  - Develop experimentally-validated modeling/simulation tools to:
    - Predict/control glass chemistry-structure-property relations.
    - Design/process tailored-property/performance FGCs.

- **Approach**
  - Characterize & model glass chemistry-structure relations.
    - Predict glass chemistry-structure relations with MD modeling.
    - Characterize glass chemistry-structure (e.g., NN distance & NMR peak shifts).
  - Characterize & model FGC processing and properties.
    - Design FGCs using composite mixing models.
    - Characterize glass & FGC wetting/interactions on stainless steel (SS).
    - Characterize glass & FGC viscosity for process modeling.
    - Predict and measure FGC properties (e.g., CTE)
  - Test, refine, & validate modeling/simulation by comparison to experiment

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

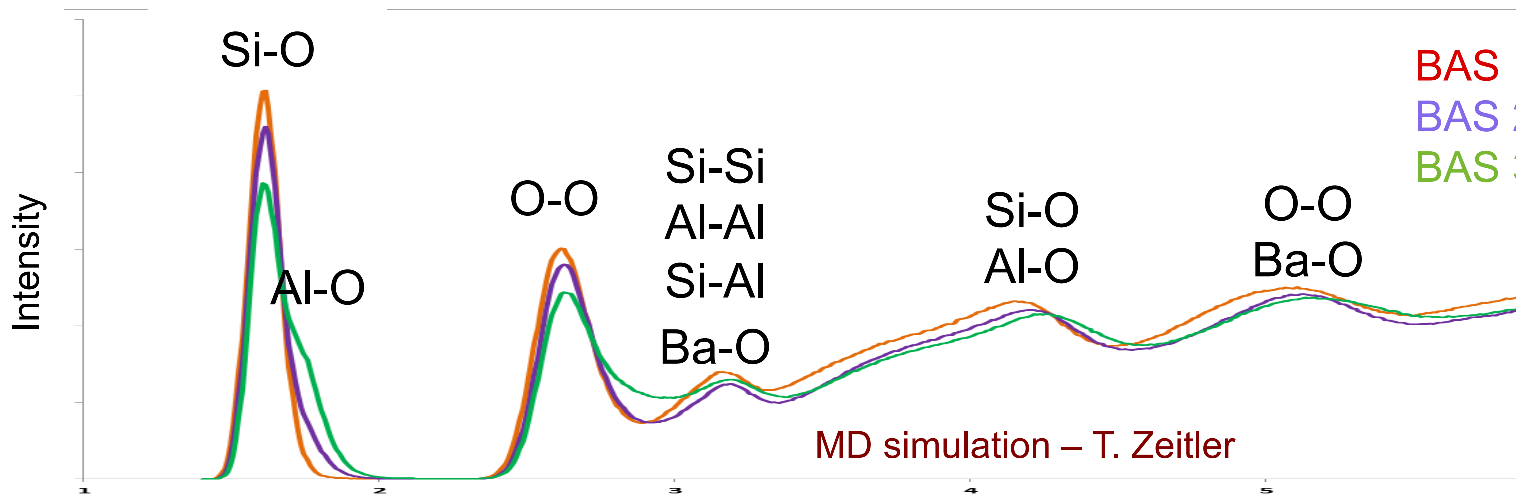


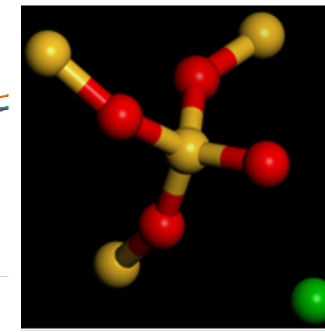
T. Zeitler

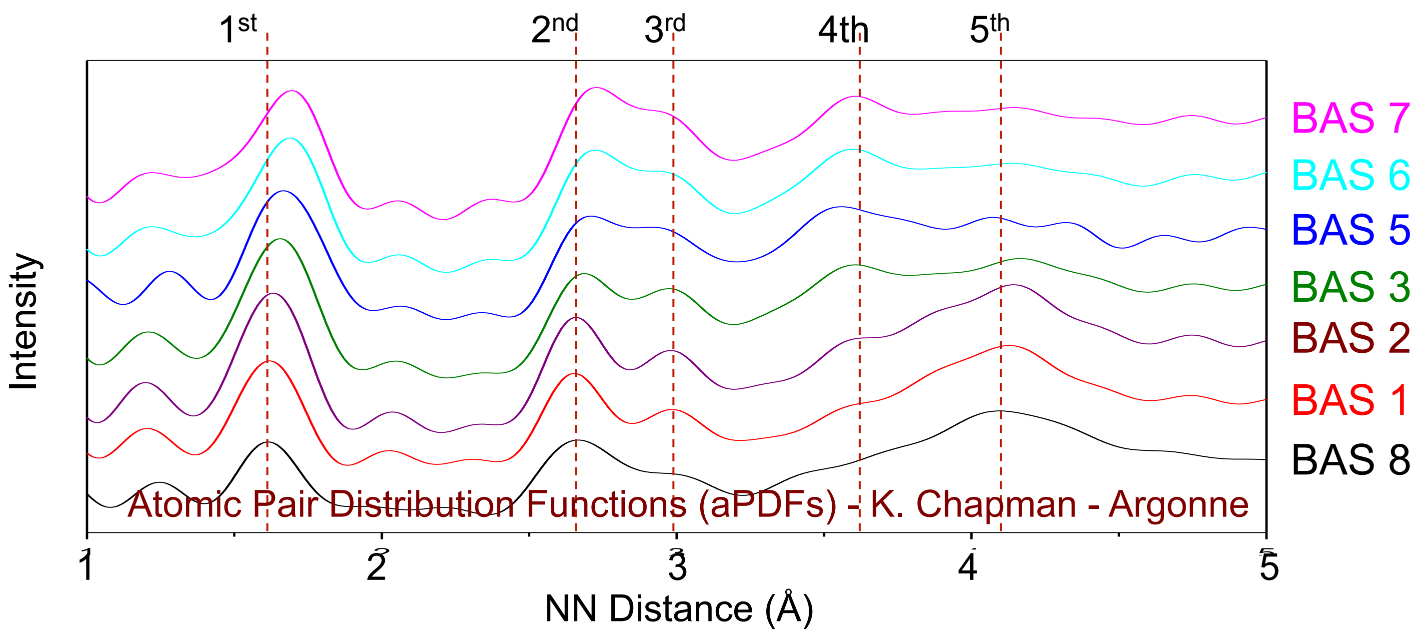
*A Pedone et al., "A new self-consistent empirical interatomic potential model for oxides, silicates, and silica-based glasses", J Phys Chem B, **110**, 11780-11795 (2006).*

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

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



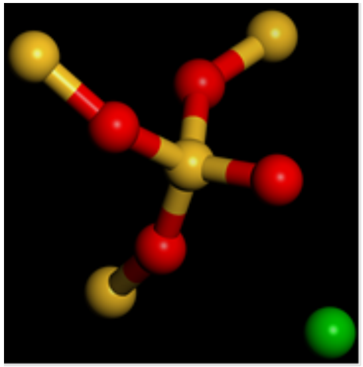




1st - Si-O & Al-O
2nd - O-Si-O
3rd - Ba-O
4th - O-Si-O-Si
5th - O-Al-O-Si-O
Ba-Ba

Model Predictions Of Chemistry-Structure Relations Have Been Tested & Validated By Comparison To Theory

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



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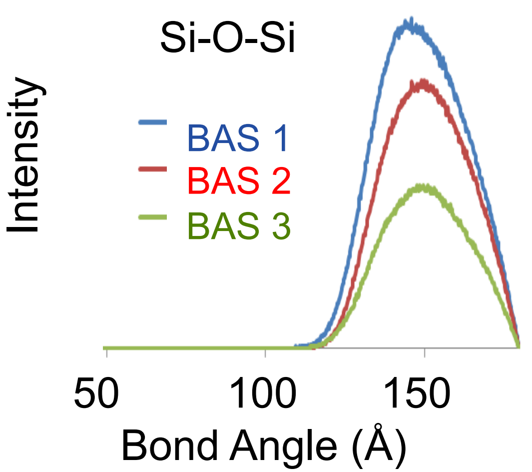
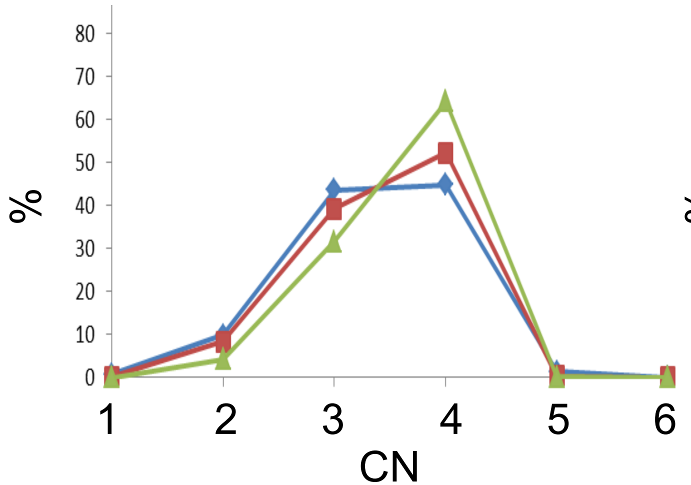
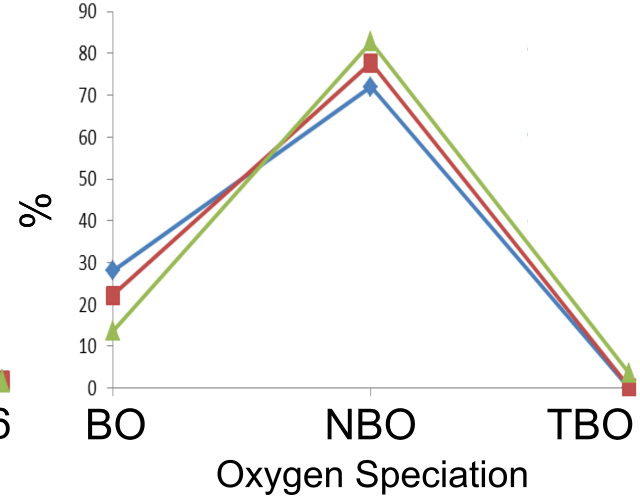
Peak position & symmetry increase from BAS 1→ 3



Q_4/Q_3 increases from BAS 1→3 (with decreasing NBOs)



BOs:NBOs increases from BAS 1→3

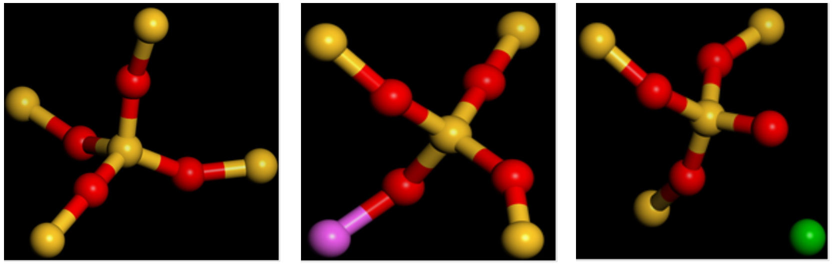


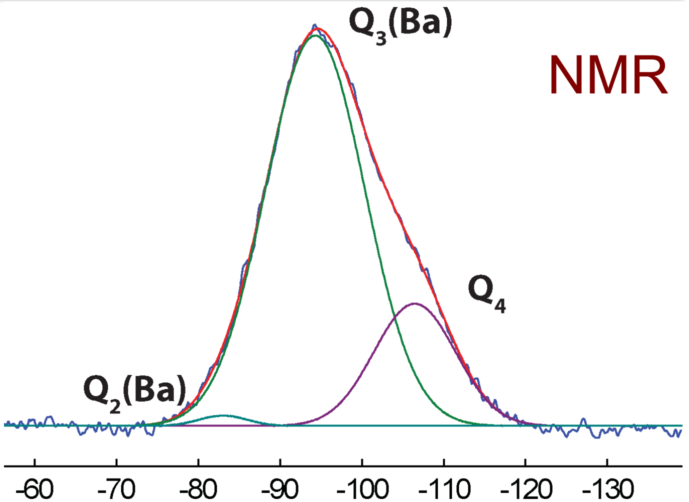
^{29}Si MAS-NMR Q_3 & Q_4 Peaks Have Been Accurately Predicted From MD Coordinates

Si(OSi)$_4$
δ = -102.1 ppm

Si(OSi)$_3$Al
δ = -74.4 ppm

Si(OSi)$_3$Ba
δ = -92.5 ppm





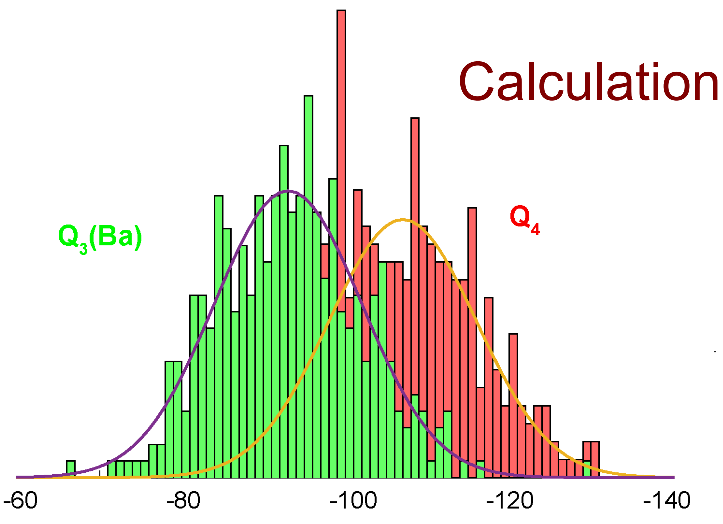
- Calculated ^{29}Si chemical shifts using MD coordinates.
- Employed correlation from Sherrif et al. (1991) based on silicate mineral structures.
- Factors included bond valence (s_i), angle of the bridging oxygen, Si-O bond distance, and distance to the 2nd nearest neighbors.

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

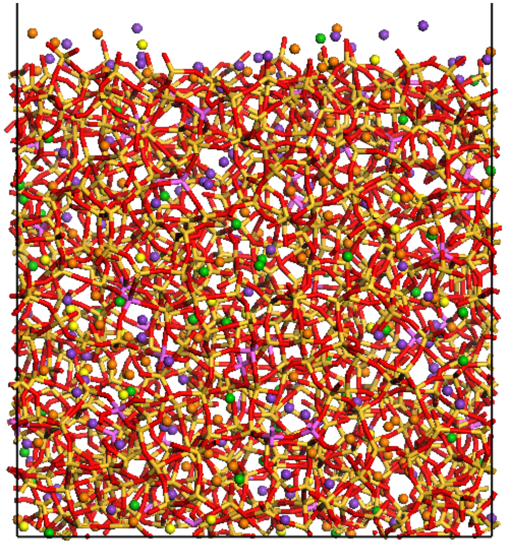
$$\Omega = \sum_{i=1}^{N}\left[s_i\left(1-3\cos^2\theta_i\right)/3R_i^3\right]\log D_i$$

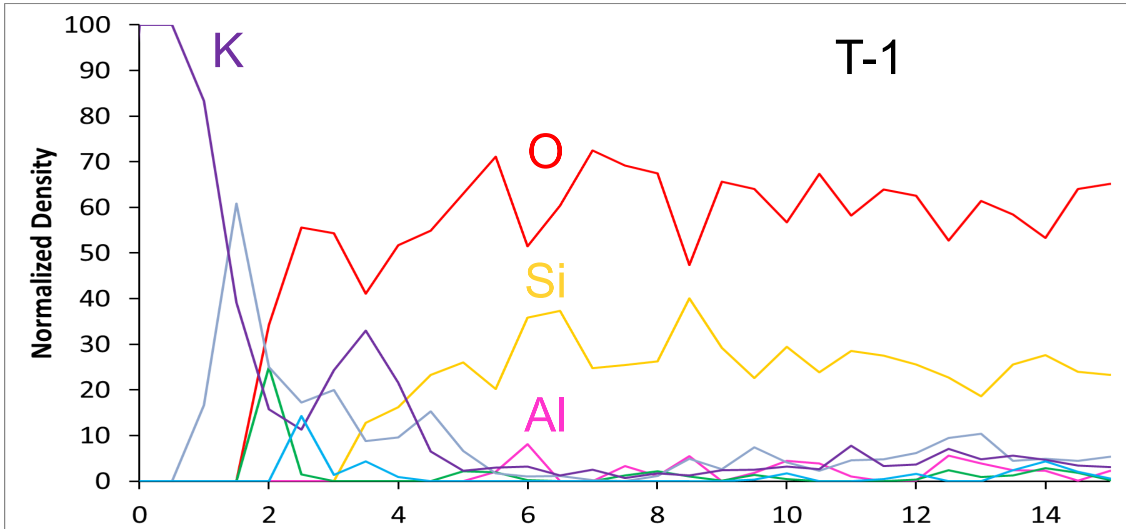
$$\delta(^{29}\mathrm{Si}) = 701.6\Omega - 45.7$$

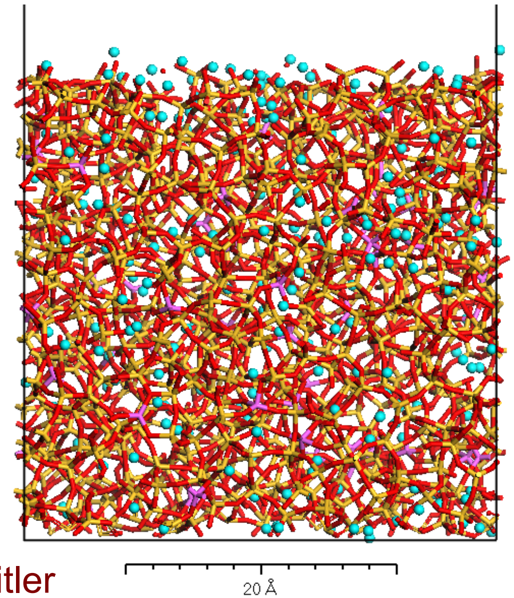
T. Alam

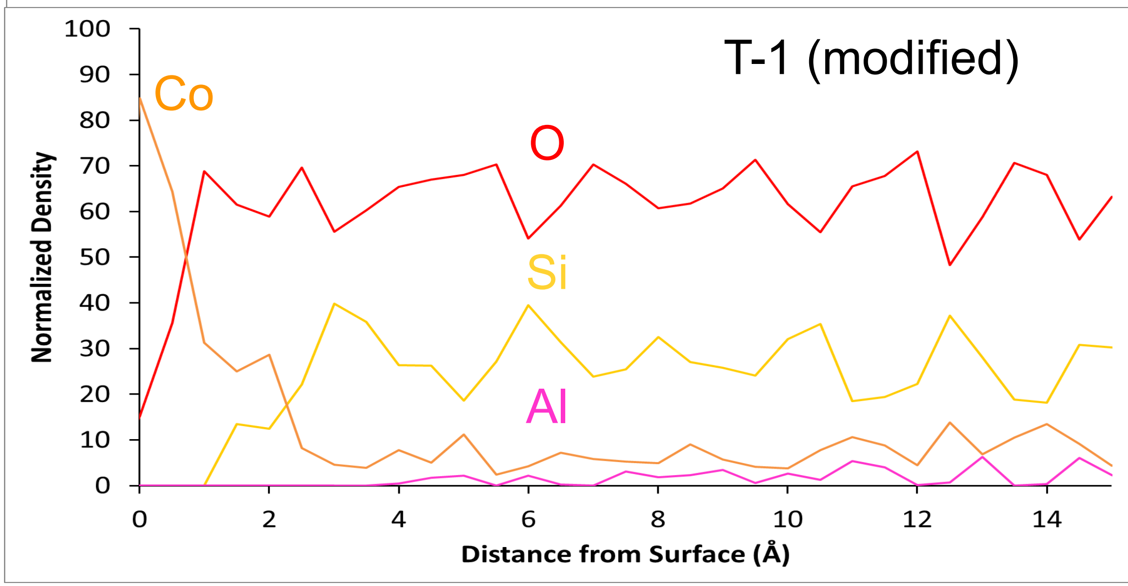


MD Simulations Show A Higher Relative Concentration Of Glass Network Modifiers On The Glass Surface









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The Relationship Between Viscosity & Filler Loading Has Value For Mitigating Reactivity And Process Modeling

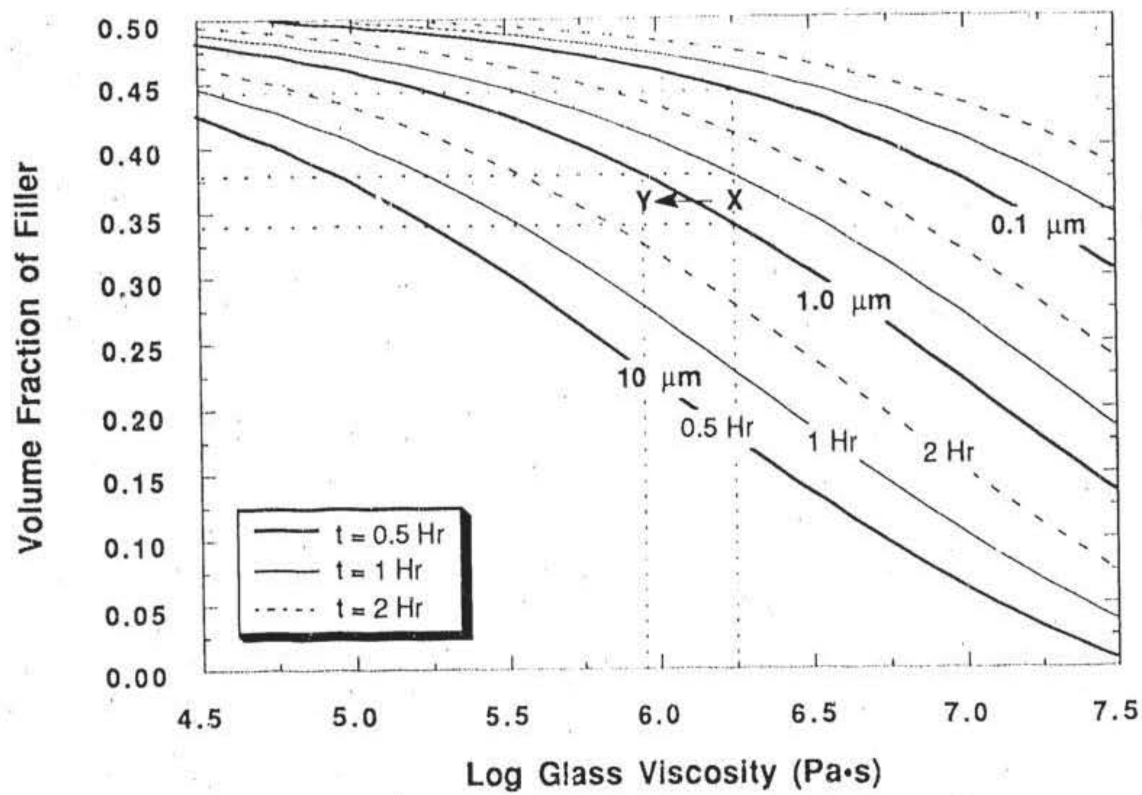
Euler's Model

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

NLPS Model

$$\eta_{s_{crit}} = \frac{t\,\gamma_{1v}}{2 r_o \left\{1 - \sqrt[3]{1 - \frac{\rho_t - 0.92}{0.08}}\right\}}$$

FGC Process Map

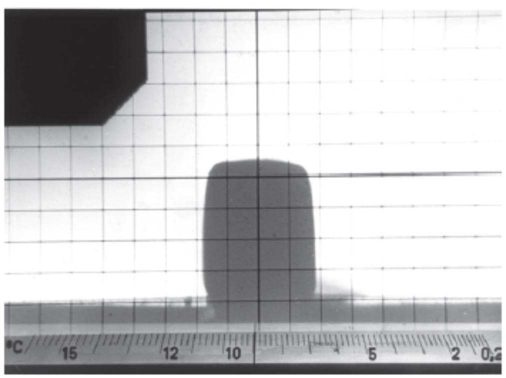


Ewsuk & Harrison, Ceramic Trans, 1991

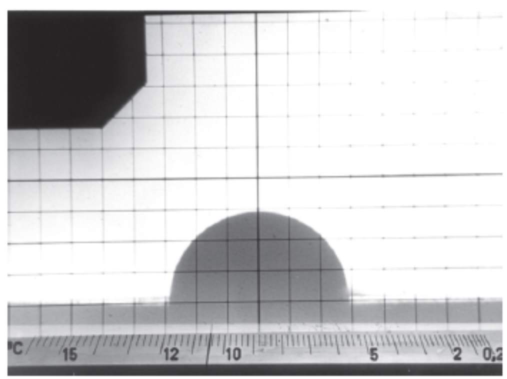
Sessile Drop Experiments Were Used To Measure Glass And FGC Wetting/Reactivity And Viscous Behavior

1. **First shrinkage or sintering**: Temperature pressed sample starts to shrink ($\log\eta$=10·0±0·3 P).
2. **Point of maximum shrinkage**: Temperature of maximum sample shrinkage before it starts to soften ($\log\eta$=8·2±0·5 P).
3. **Softening point**: Temperature of first signs of softening (disappearance or rounding of edges of the sample ($\log\eta$=6·1±0·2 P).
4. **Half ball point**: Temperature at which sample forms a ($\log\eta$=4·6±0·1 P).
5. **Flow point**: Temperature of maximum height of the drop of molten glass ($\log\eta$=4·1–4·3 P).

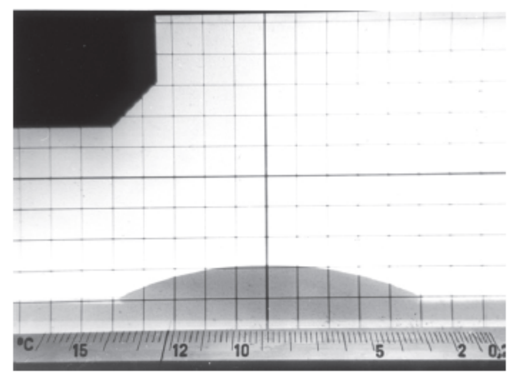
Scholze, "Influence of viscosity and surface tension on hot-stage microscopy measurements on glasses," *Ver. Dtsch. Keram. Ges*., 1962, **391**, 63–8.)



Softening Point



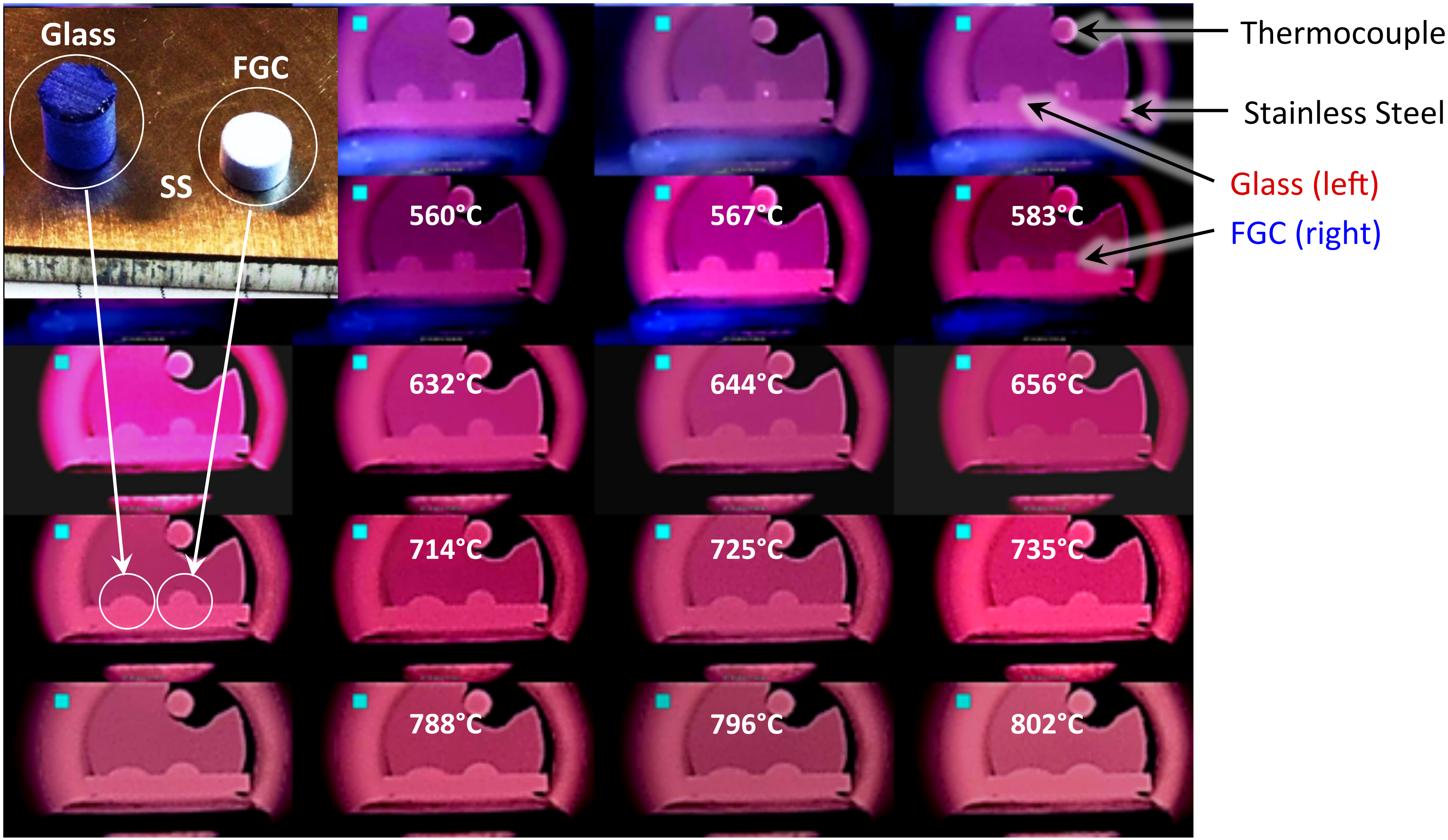
Half Ball Point



Flow Point

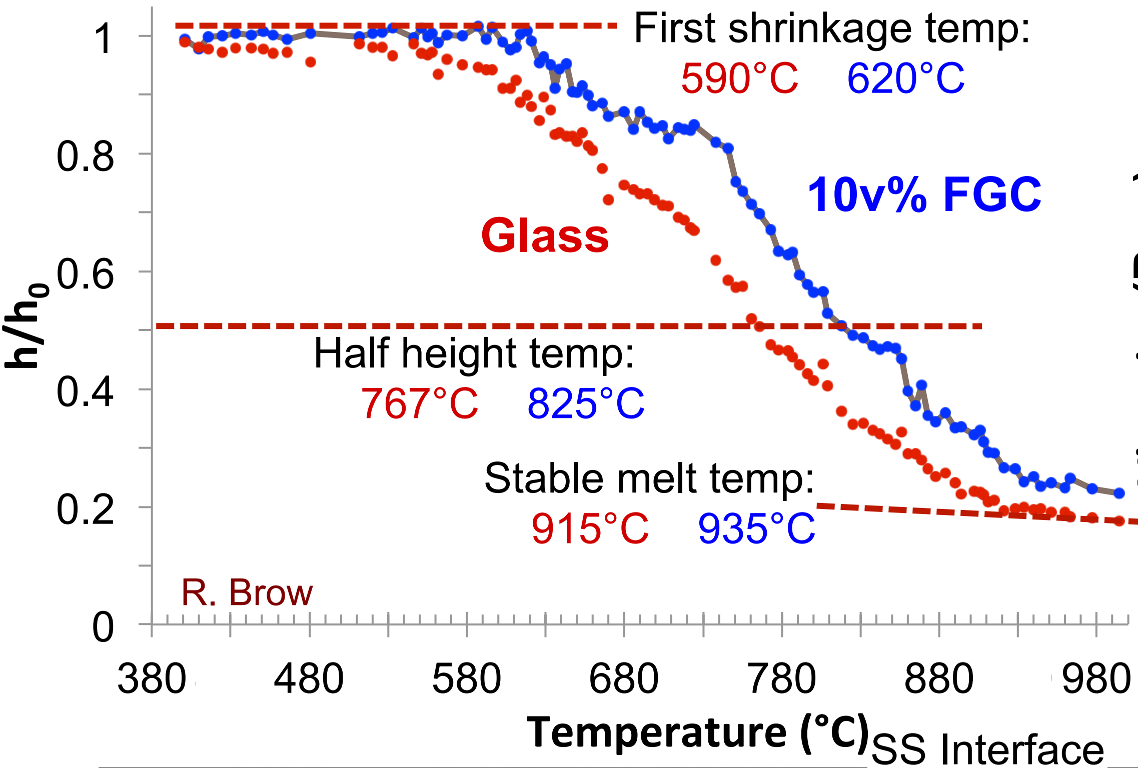
Pascual, et al., Phys. Chem. Glasses (2001) 42[1] 61-66.

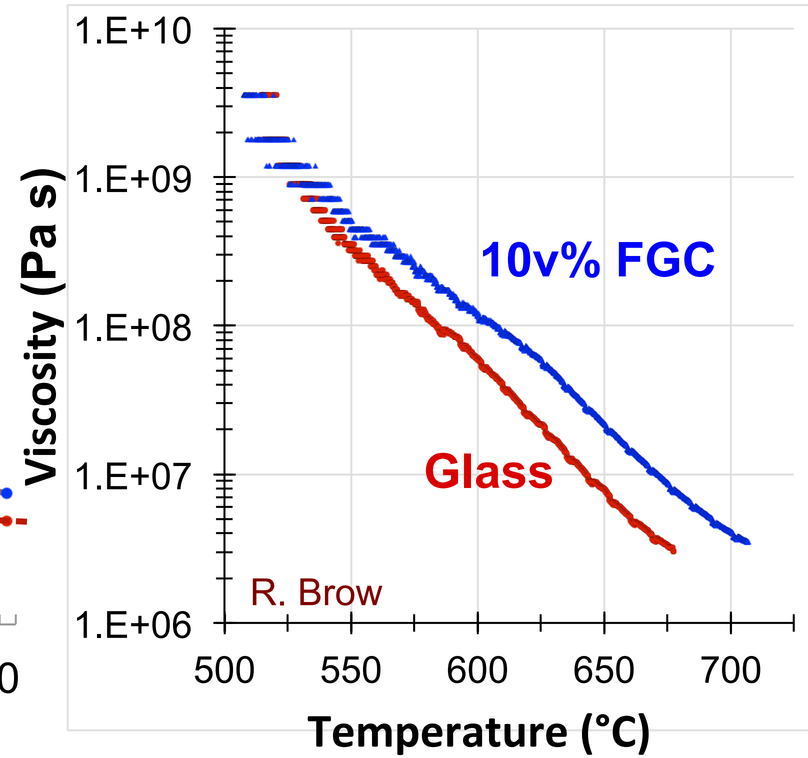
Wetting & Viscous Flow Were Characterized Using Sessile Drop Experiments On Stainless Steel

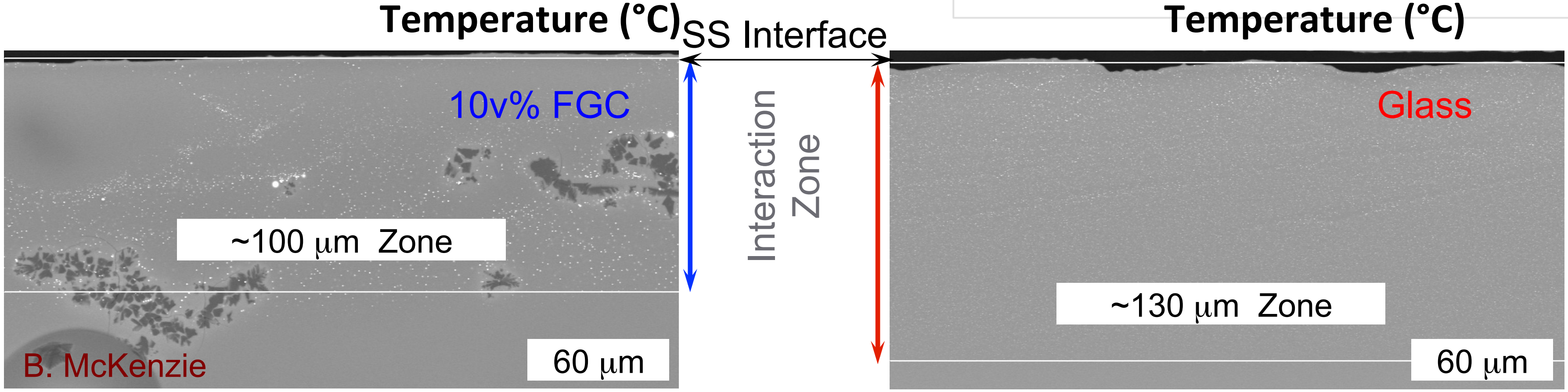


Prof. R Brow – MO U S&T

The Filler Addition Increases The FGC Viscosity And Decreases FGC Reactivity Relative To The Glass

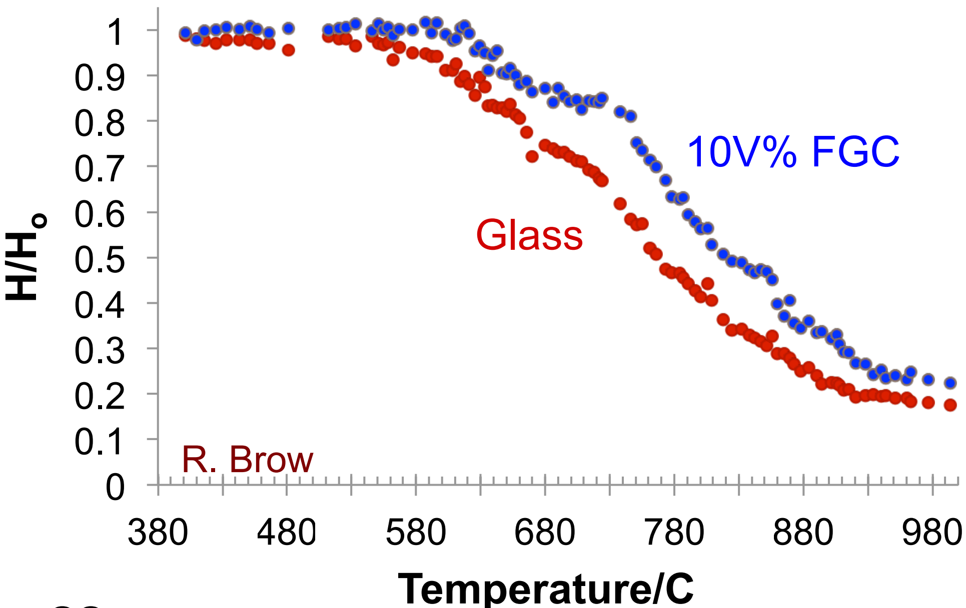




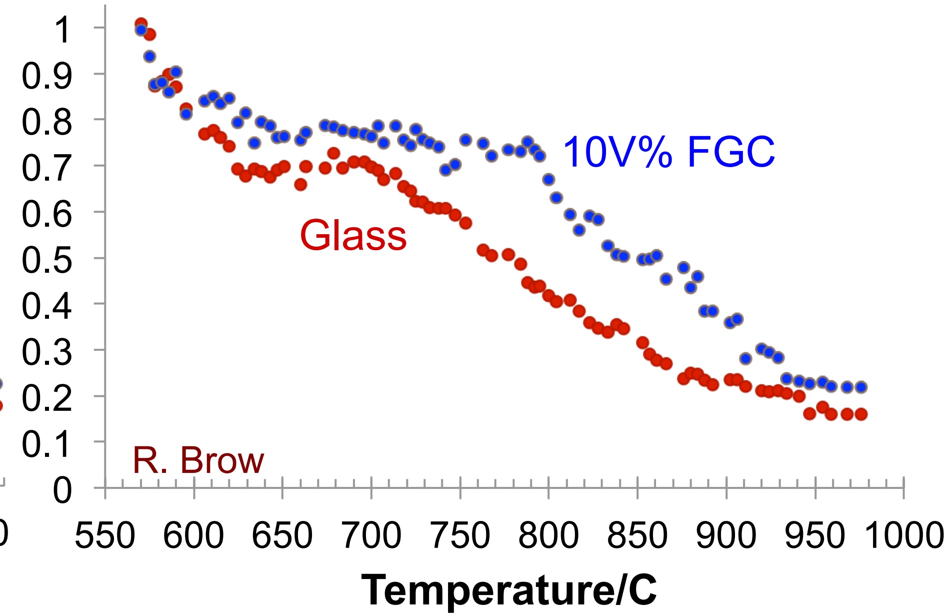


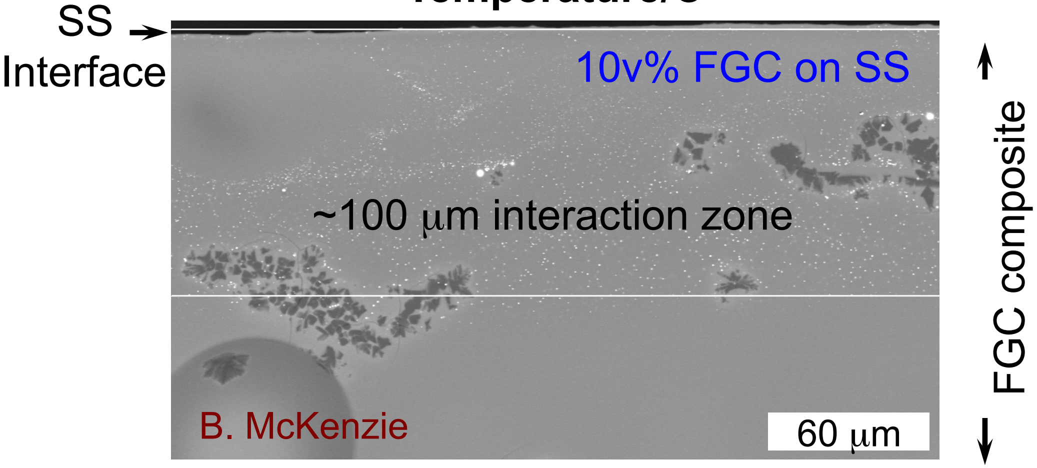
Wetting And Reaction Are Initially Enhanced On The Oxidized The Stainless Steel Surface

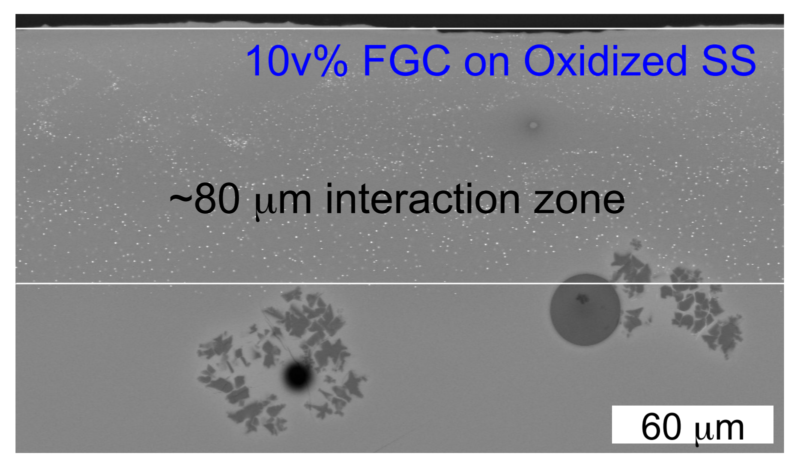
Wetting on SS



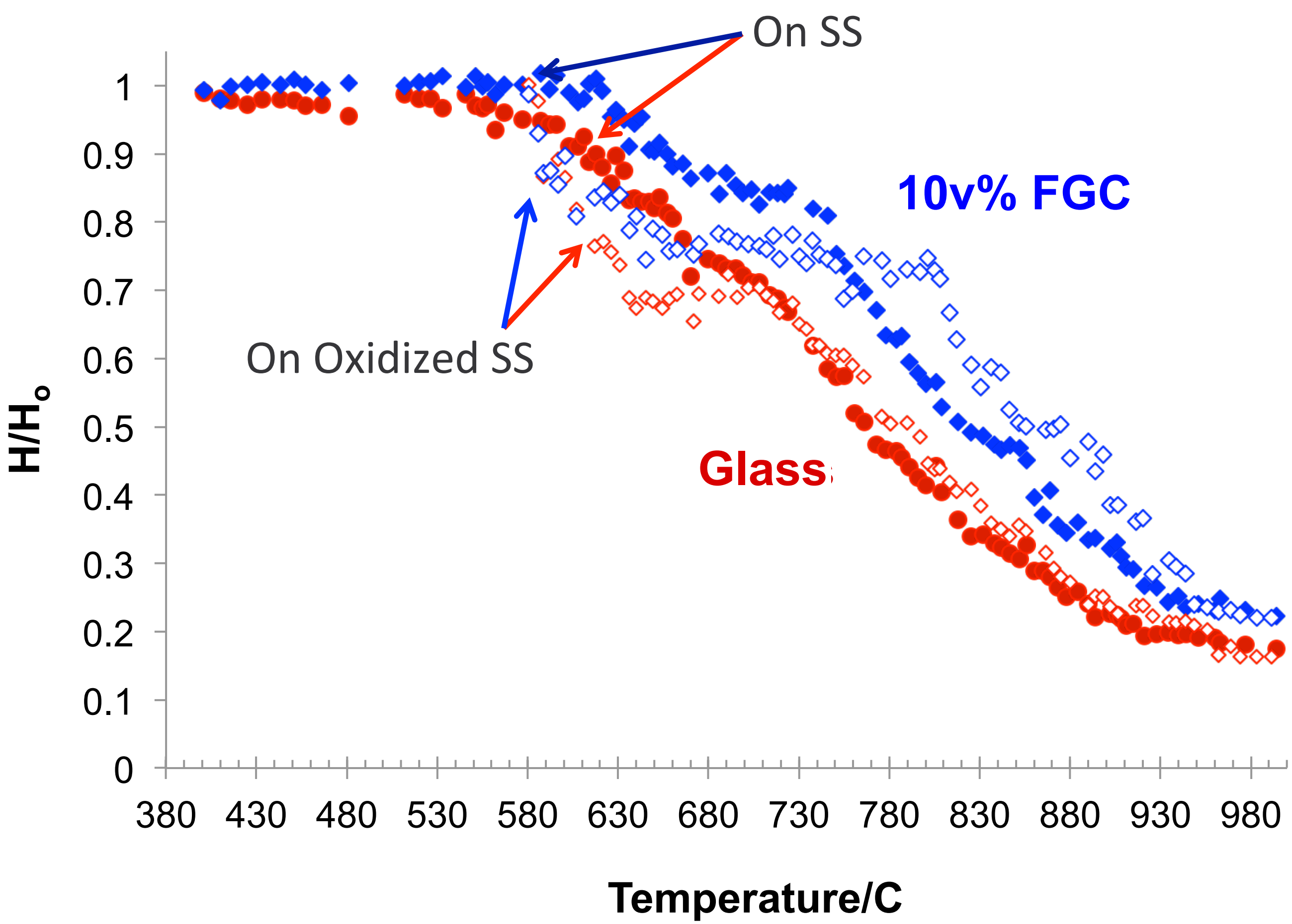
Wetting on Oxidized SS





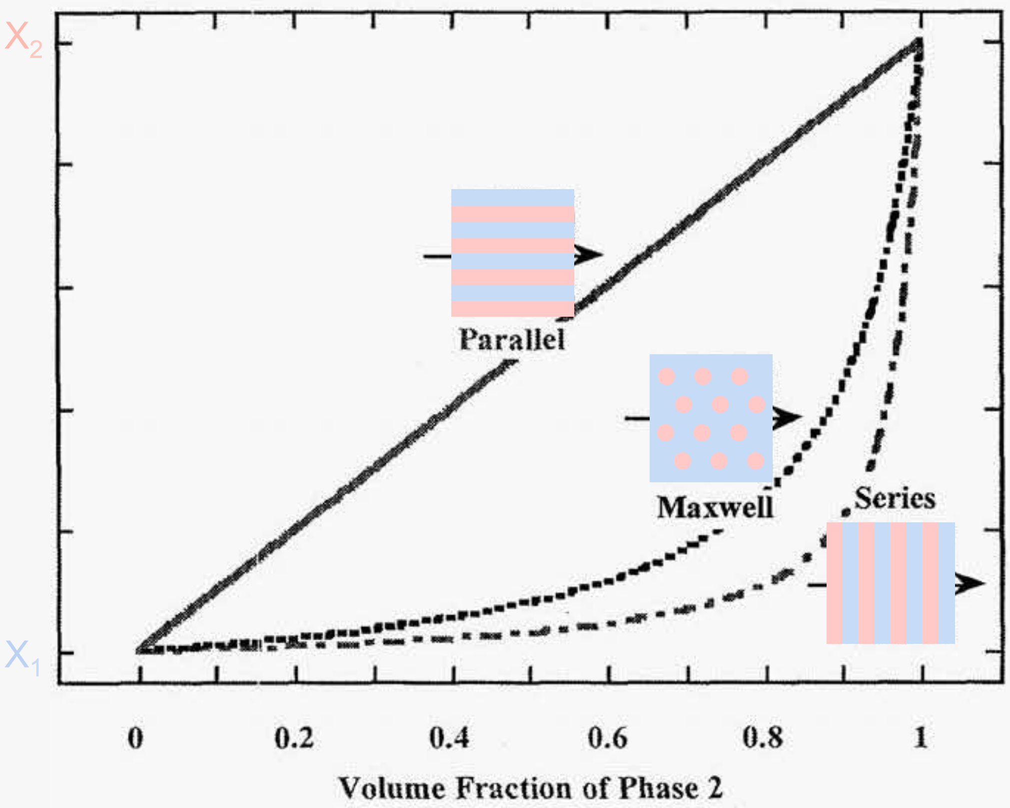


FGC Reactivity Is Reduced After The Initial Oxide Layer Is Dissolved



Process & Property Modeling Will Be Used To Design Manufacturable, Tailored-Property FGCs

Validated FGC Property Models



Parallel Mixing Model

$$X_{Comp} = X_1 f_1 + X_2 f_2$$

Series Mixing Model

$$X_{Comp} = \frac{X_1 X_2}{X_1 f_2 + X_2 f_1}$$

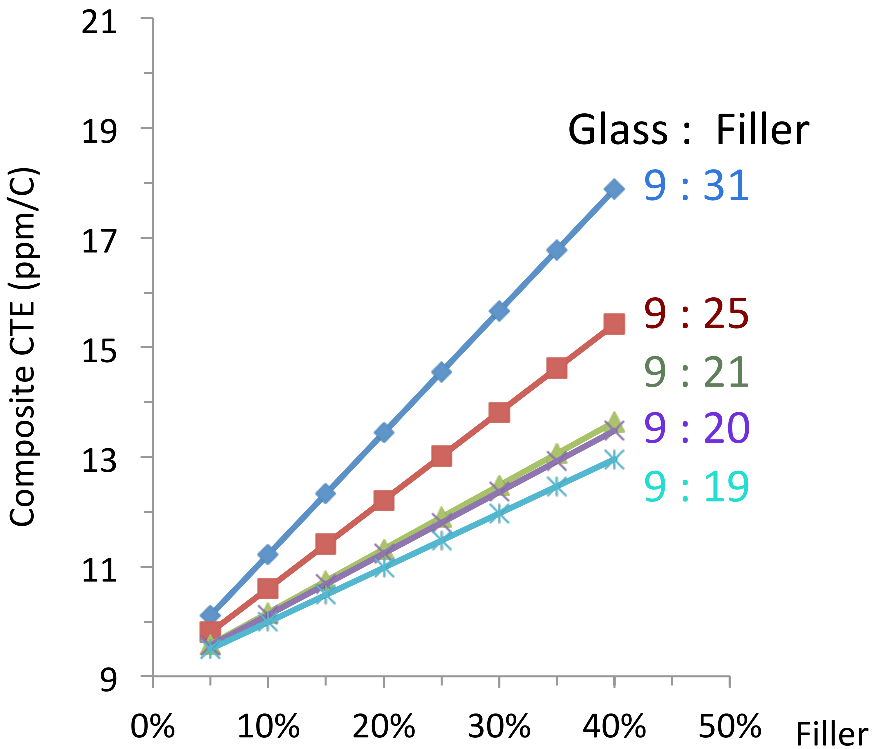
Series Mixing Model

$$X_{Comp} = \frac{X_m f_m \left(\frac{2}{3} + \frac{X_d}{3X_m} \right) + X_d f_d}{f_m \left(\frac{2}{3} + \frac{X_d}{3X_m} \right) + f_d}$$

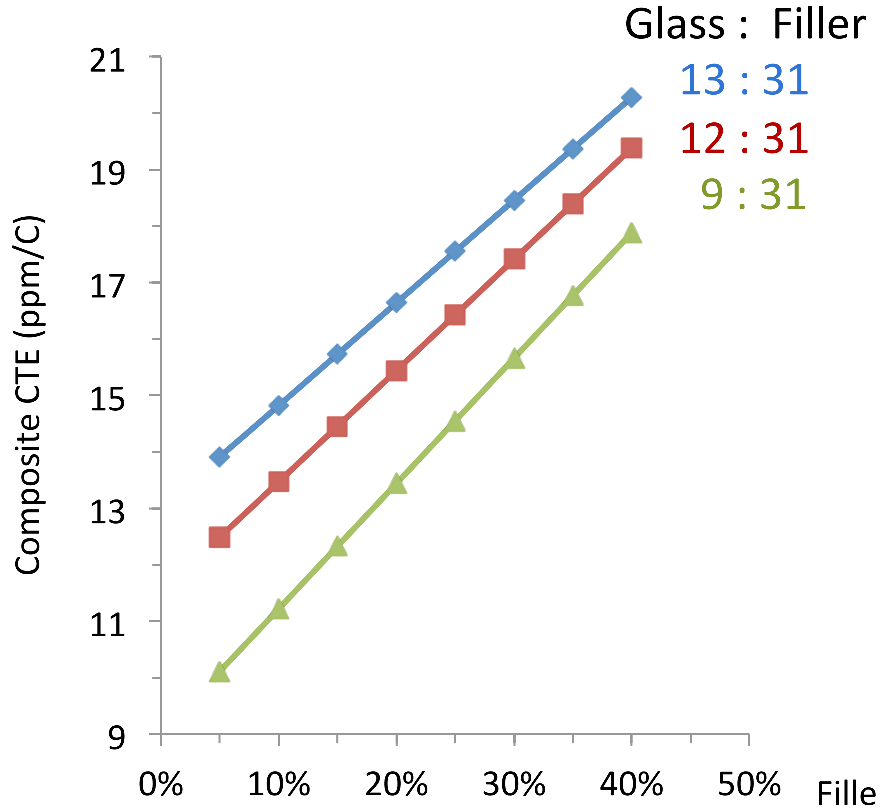
Ewsuk & Harrison, Ceramic Trans, 1995

The Glass Matrix CTE Is Critical To Achieving A Manufacturable, High CTE FGC

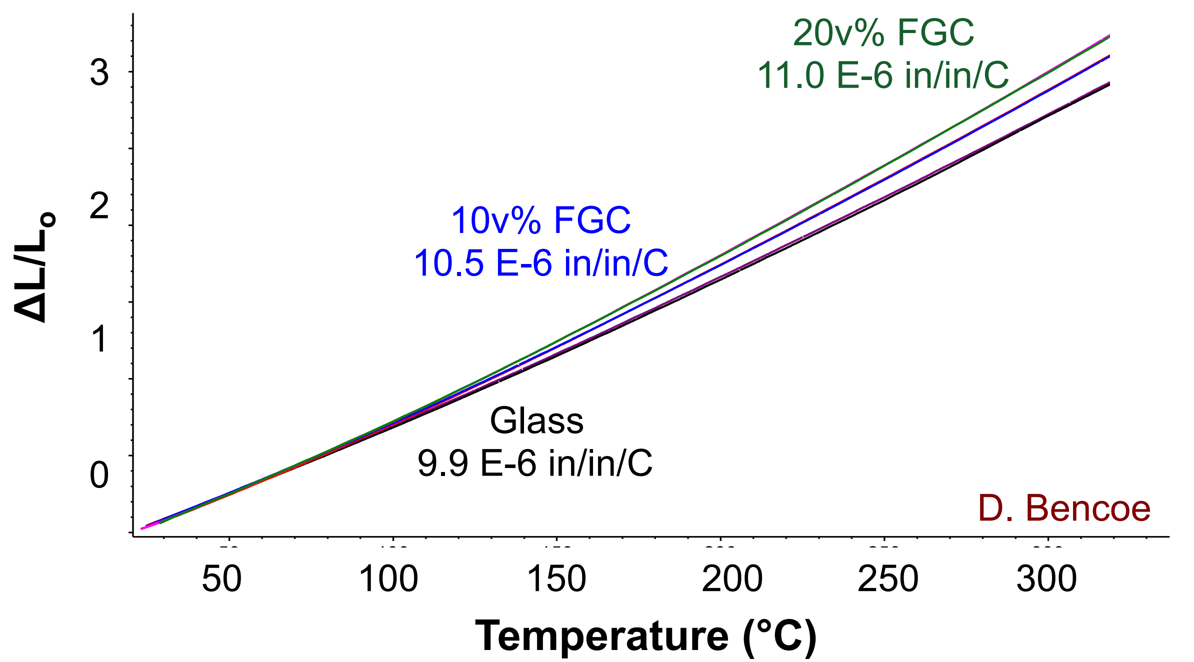
Effects of Filler CTE



Effects of Glass/Matrix CTE



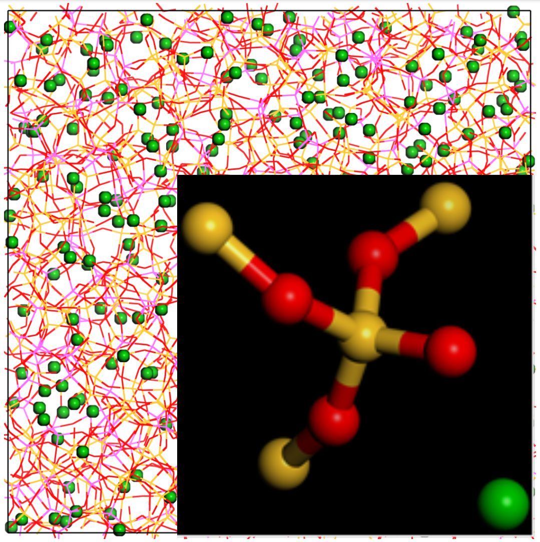
Filled-Glass Composite (FGC) Properties Are Tunable Are Consistent With Model Predictions



Material	Measured CTE (ppm/C)	Predicted CTE (ppm/C)
Glass	9.9	----
10v% FGC	10.5	10.4
20v% FGC	11.0	11.0
17.5v% FGC	17.0	16.9

Experimentally-Validated Modeling Is Being Developed To Enable Advanced FGC Design And Fabrication

- **Glass Chemistry-Structure Relations Have Been Modeled**
  - Good first-order agreement between experiments and MD model bulk structures
    - Modeling is an efficient means to assess bulk glass chemistry-structure relations
  - Initial interface modeling results are consistent with expectations



- **Tailored Property FGCs Have Been Designed, Fabricated, & Characterize.**
  - Measured FGC CTE trends as predicted by modeling
  - Initial wetting & reactivity results are consistent with modeling/expectations
    - FGCs have higher viscosity and lower reactivity relative to glass
    - Initial wetting & reactivity are enhanced on oxidized SS