Fall 11-10-2016

Characterization and modeling to design and develop tailored-property filled glass composites

Kevin Ewsuk
Sandia National Laboratories, kgewsuk@sandia.gov

Exceptional service in the national interest

Sandia National Laboratories

LDRD
LABORATORY DIRECTED RESEARCH & DEVELOPMENT

09:50–10:10 Louise Room
Structural Composites Session I

Characterization and Modeling to Design and Develop Tailored-Property Filled-Glass Composites

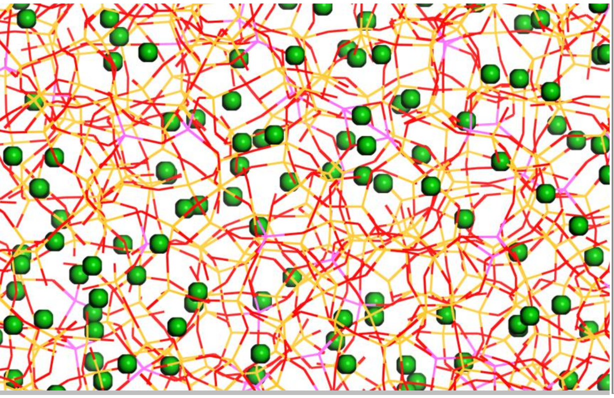
Kevin G. Ewsuk
Sandia National Laboratories
Albuquerque, NM 87185

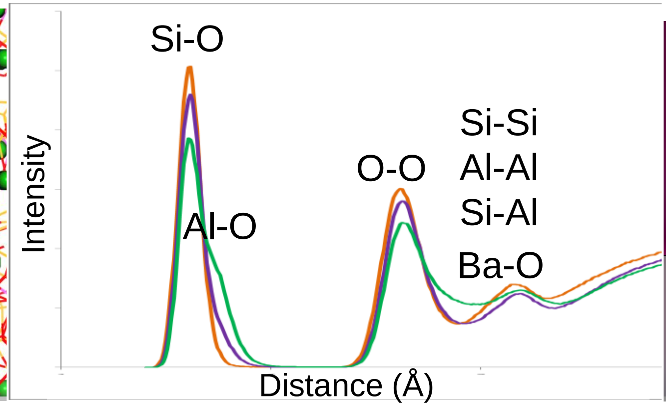
Composites at Lake Louise-2015
November 8– 12, 2015
Lake Louise, Alberta, Canada

U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

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





Todd R. Zeitler & Louise J. Criscenti - MD Modeling

Michael T. Brumbach, Mark A. Rodriguez, & Todd M. Alam - Glass Structure

Denise N. Bencoe & Bonnie McKenzie - Glass & Composite Characterization

Sandia National Laboratories

Richard K. Brow - Glass & Composite Characterization

Missouri University of Science & Technology

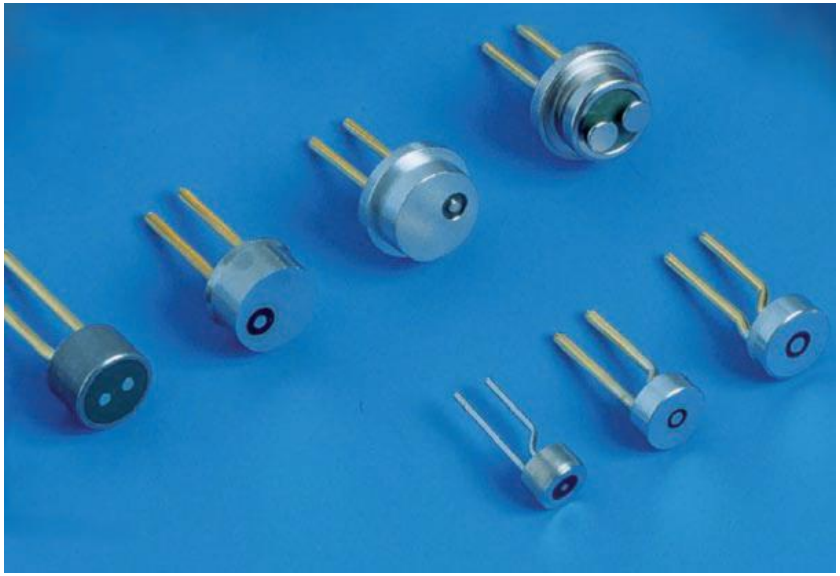
Karina Chapman - Glass Characterization

Argonne National Laboratories

Glass Is Commonly Used To Bond/Join Inorganic Materials

- **Glass bonding/joining Applications**
  - Glass-bonded composites
    - Glass-bonded alumina
  - Seals
    - Hermetic glass-to-metal (GtM) seals
      - Air bag igniters
      - Medical implants
      - Microelectronics
    - Solid oxide fuel cells (SOFCs)

*Feedthroughs for pressure & flow sensors



*Airbag igniter feedthroughs

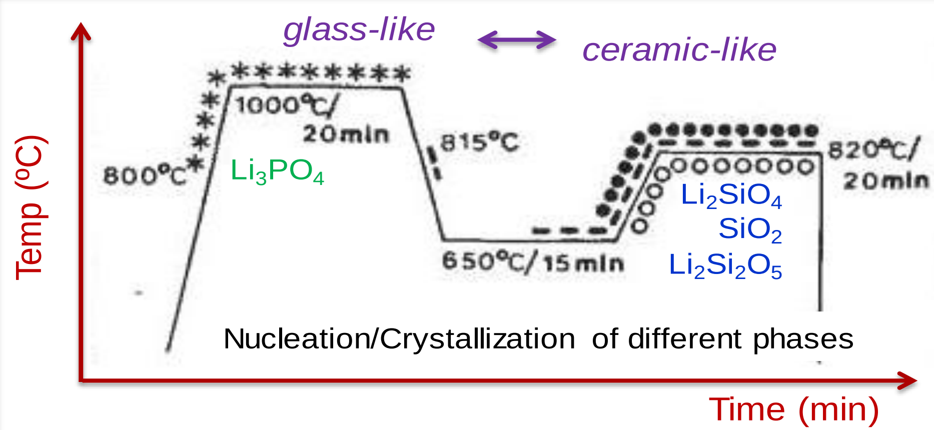
*Schott Electronic Packaging

Filled-Glass Composites (FGCs) Have The Processability Of A Glass With The Properties Of A Ceramic

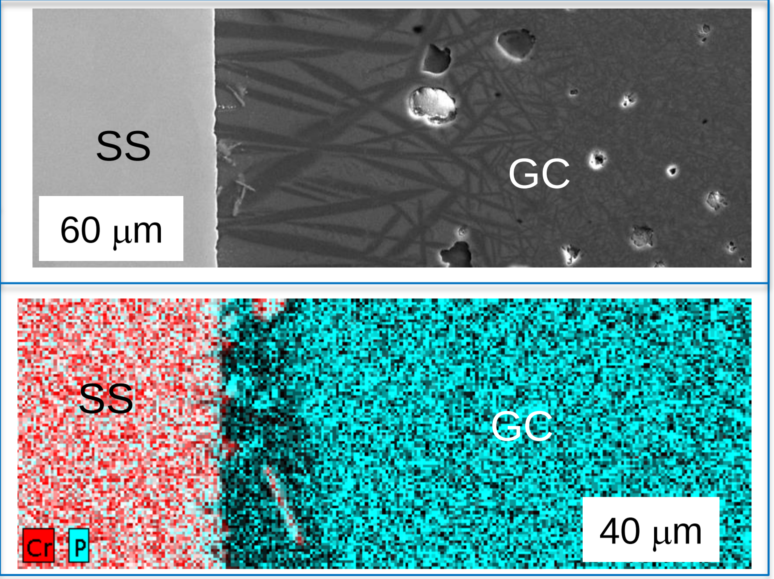
Glass
+ Processability
+ Materials compatibility
- Low/fixed CTE
- Low toughness/crack tolerance

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).



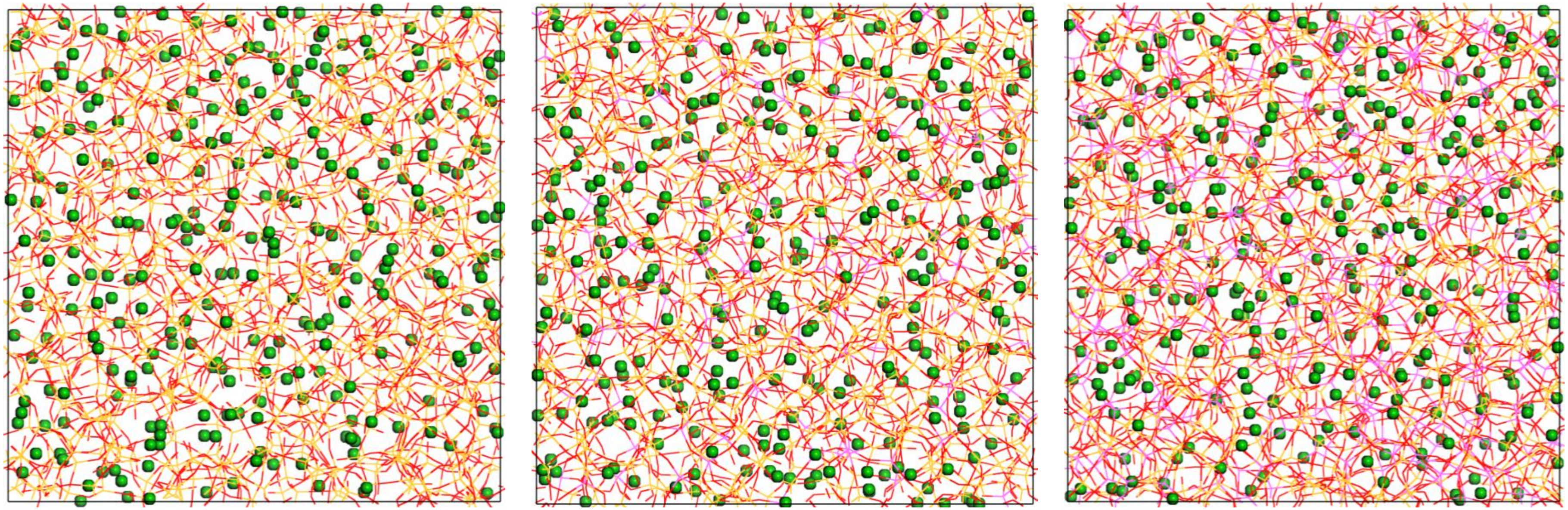
Materials Science & Engineering Are Being Developed To Design/Develop Advanced Filled-Glass Composites

- **Objectives**
  - Develop experimentally-validated modeling/simulation tools to:
    - Predict/control glass chemistry-structure-property relations.
    - Design & process filled-glass composites (FGCs).
- **Approach**
  - Characterize & model glass chemistry-structure-property relations.
    - Predict glass chemistry-structure relations with MD modeling.
    - Characterize glass chemistry-structure (NN distance & NMR peak shifts).
  - Characterize & model FGC processing & properties.
    - Design FGCs using mixing models.
    - Characterize glass & FGC wetting/interactions on stainless steel (SS).
    - Characterize glass & FGC viscosity for process modeling.
  - Test, refine, & validate modeling/simulation by comparison to experiment

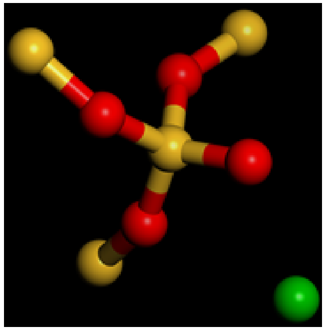
BAS Glasses Were Simulated With The LAMMPS** MD Code & Pedone* Multicomponent Force Field

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

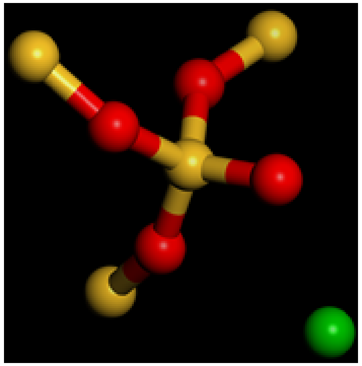


A Pedone et al., "A new self-consistent empirical interatomic potential model for oxides, silicates, and silica-based glasses", J Phys Chem B, **110, 11780-11795 (2006).*

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

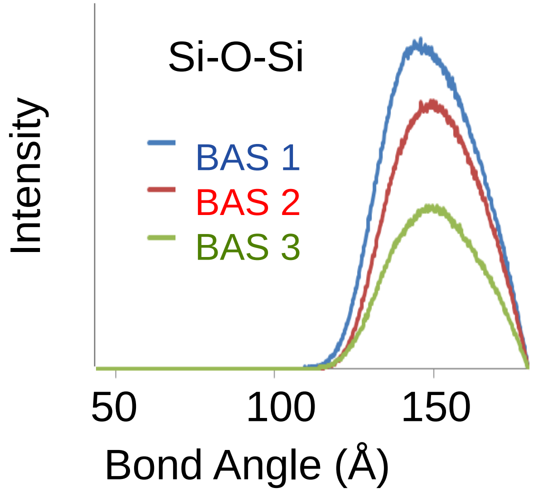
Model Predictions Of Chemistry-Structure Relations Were Tested & Validated By Comparison To Theory

Glass	g/mole	Mole % Al_2O_3	NBO_{Th} (%)	NBO_{MD} (%)	$Connectivity_{Th}$ (BO/NF)
BAS 8	91.1	0	40.0	39.5	1.50
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

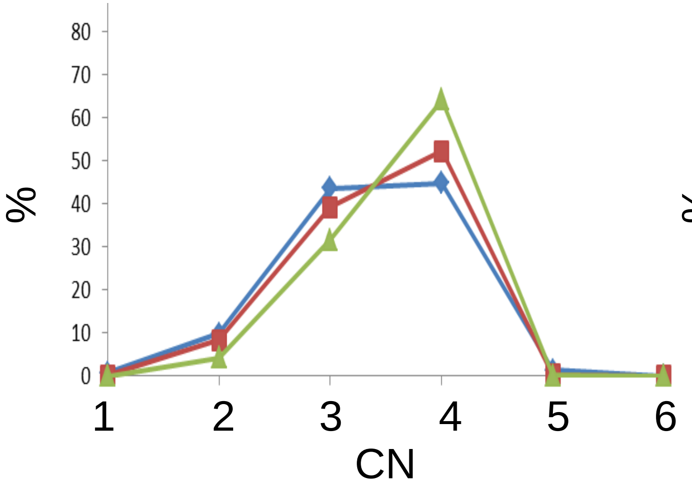


T. Zeitler

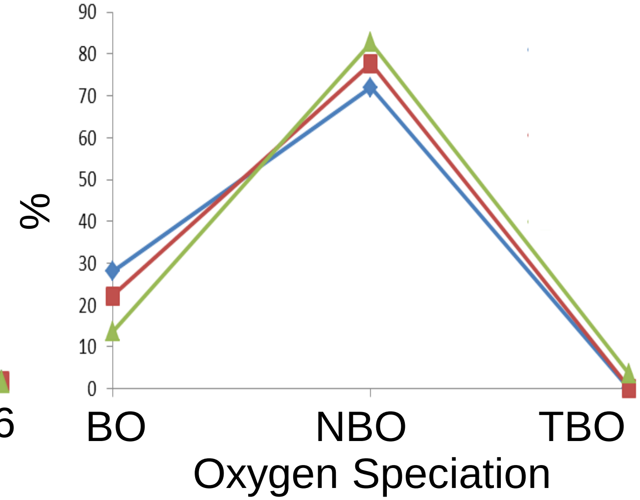
Peak position & symmetry increase from BAS 1→ 3



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



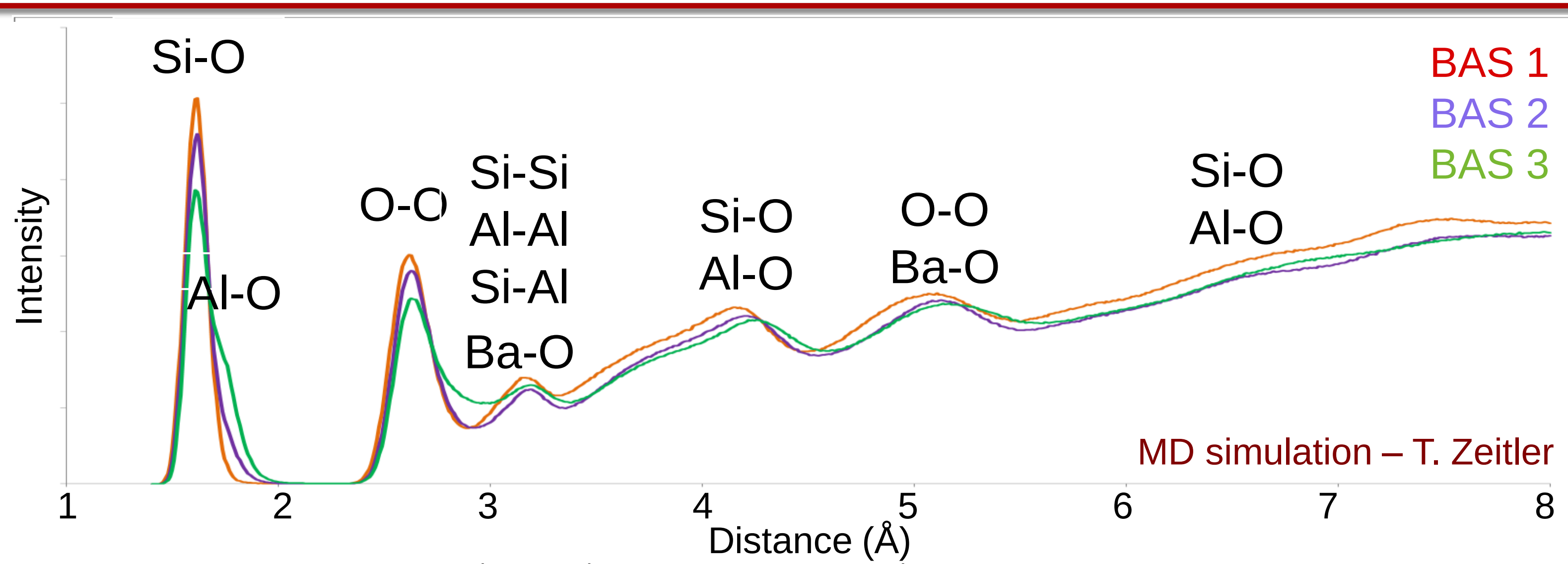
BOs:NBOs increases from BAS 1→3

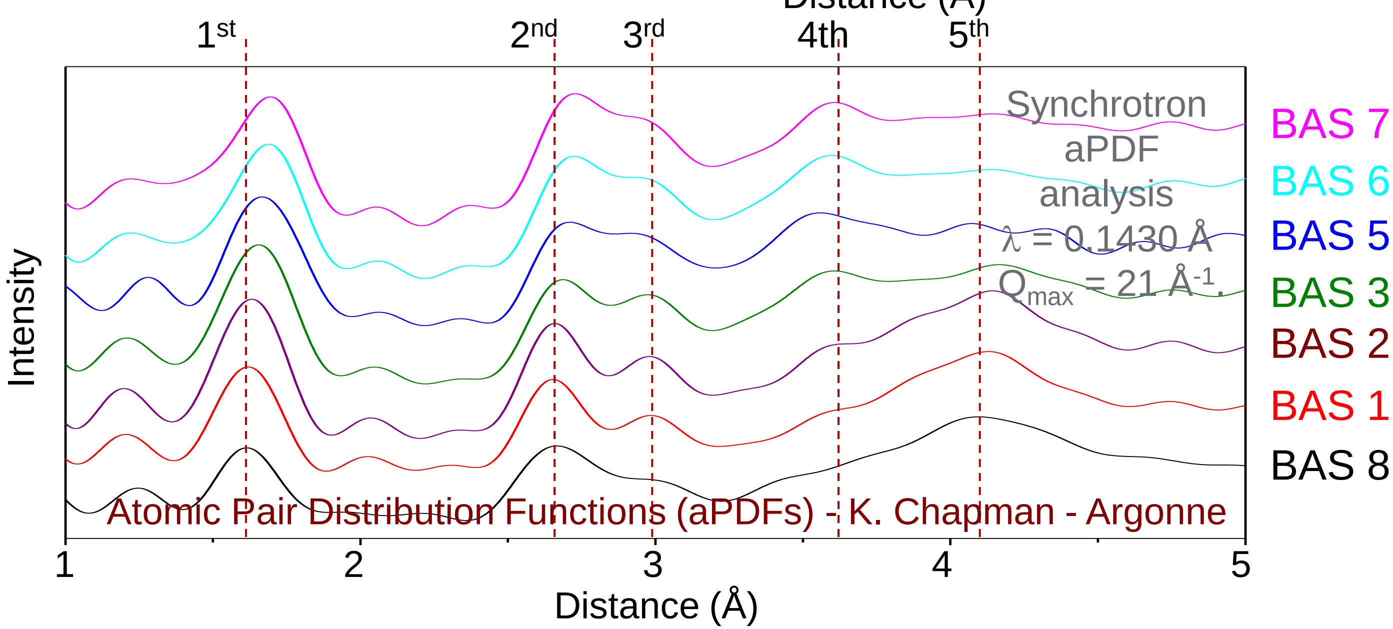


Model Predictions Of Glass Chemistry-Structure Were Tested & Validated By Comparison To Experiment

Tool	Nearest Neighbor (NN) Distances	NN Assignments	Coordination Number (CN)	Non-Bridging Oxygens (NBOs)	Glasses
Model	Y	Y	Y	Bond Angle Distributions, BO's/ NBO's	BAS 1-3,8
aPDF	Y	Inferred from crystallography			BAS 1-3,8
NMR	Trends for Si & Al			Order/Disorder Trends	BAS 1-3,8
EXAFS	Y	Y (Ba)	Y (Ba)		BAS 1-3,8

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



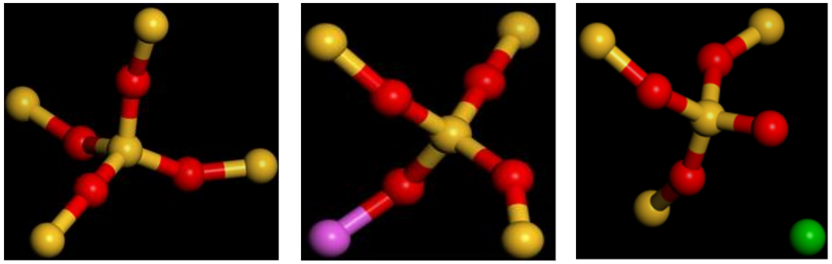


1st - Si-O & Al-O
2nd - O-Si-O
3rd - Ba-O
4th - O-Si-O-Si
5th - O-Al-O-Si-O
Ba-Ba

M. Rodriguez

^{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)$_3$Al δ = -74.4 ppm | Si(OSi)$_3$Ba δ = -92.5 ppm



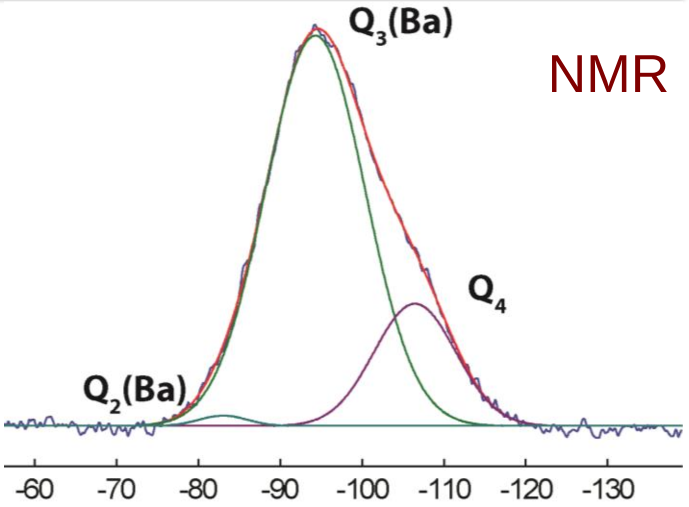
- Calculated ^{29}Si chemical shifts using MD coordinates.
- Employed correlation from Sherrif et al. (1991) based on silicate mineral structures.
- Factors included bond valence (s_i), angle of the bridging oxygen, Si-O bond distance, and distance to the 2nd nearest neighbors.

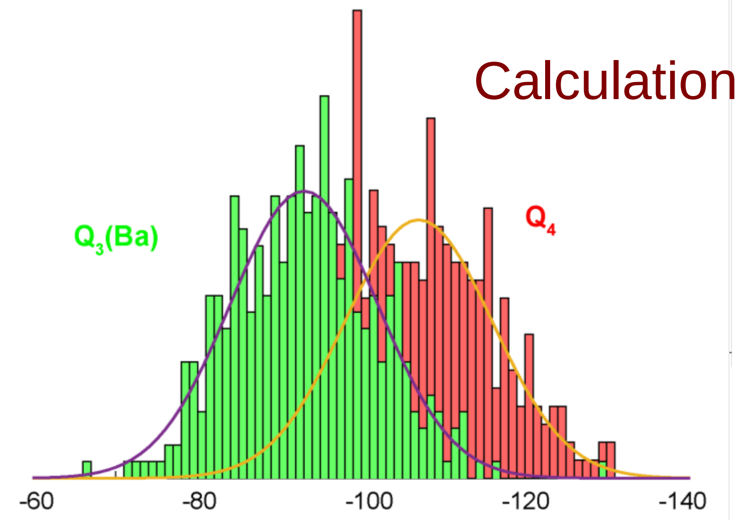
$$s_i = \left(\exp\left[\left(r_0 - r_i\right)/0.37\right]\right)$$

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

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

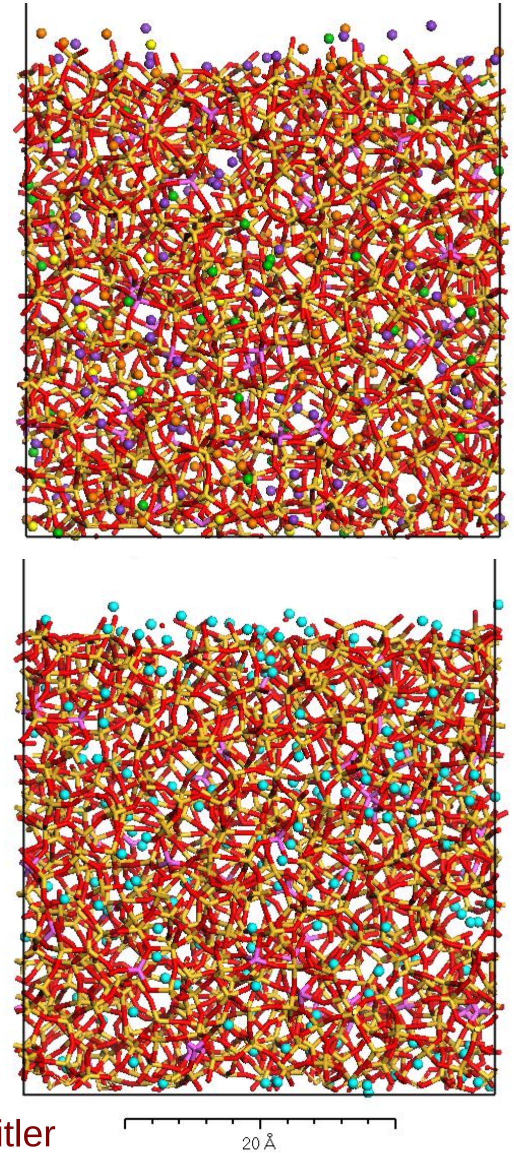
T. Alam

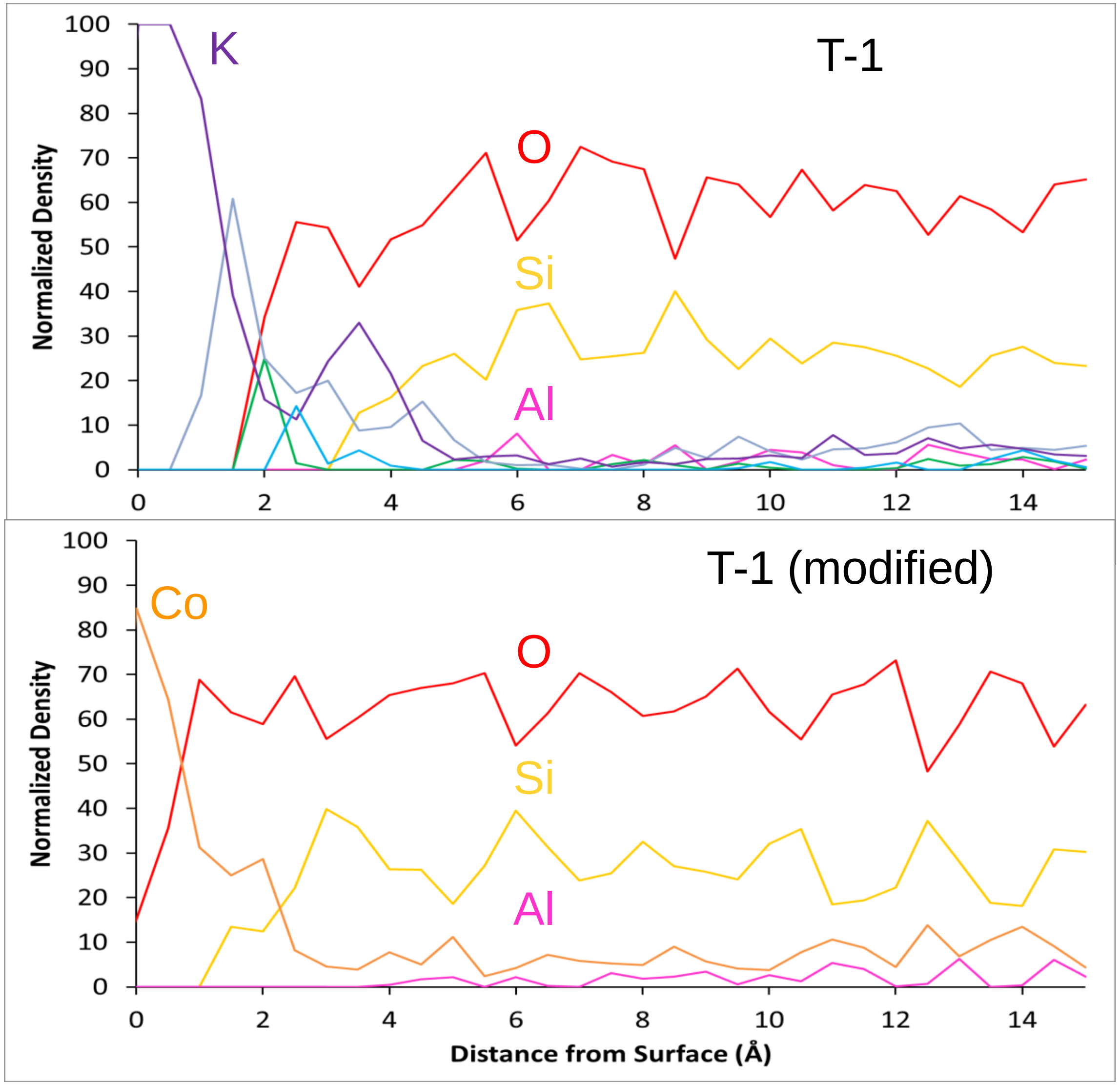




^{29}Si Chemical Shift (ppm)

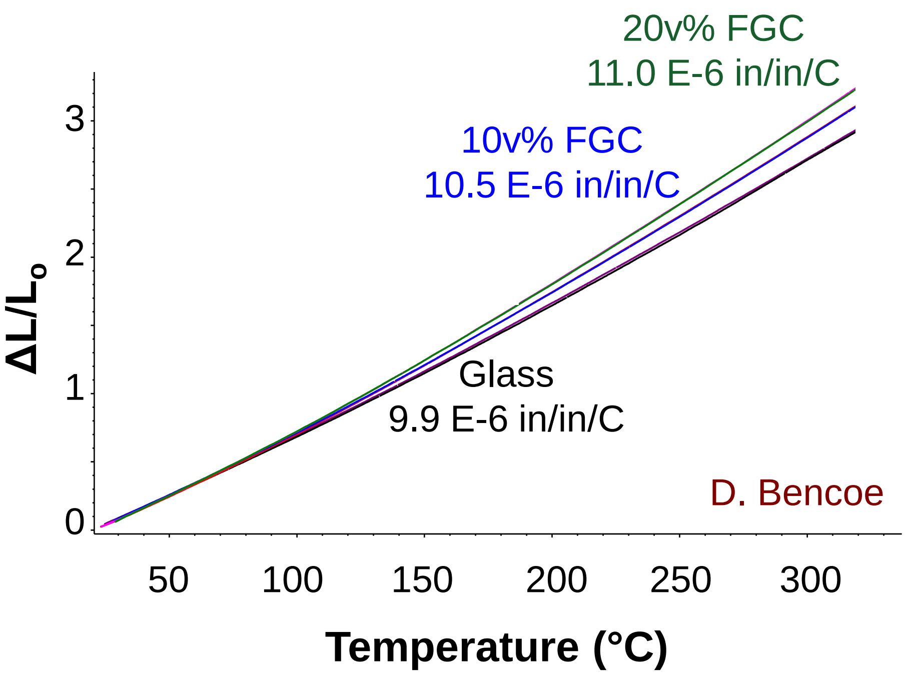
MD Simulations Show A Higher Relative Concentration Of Glass Network Modifiers On The Glass Surface

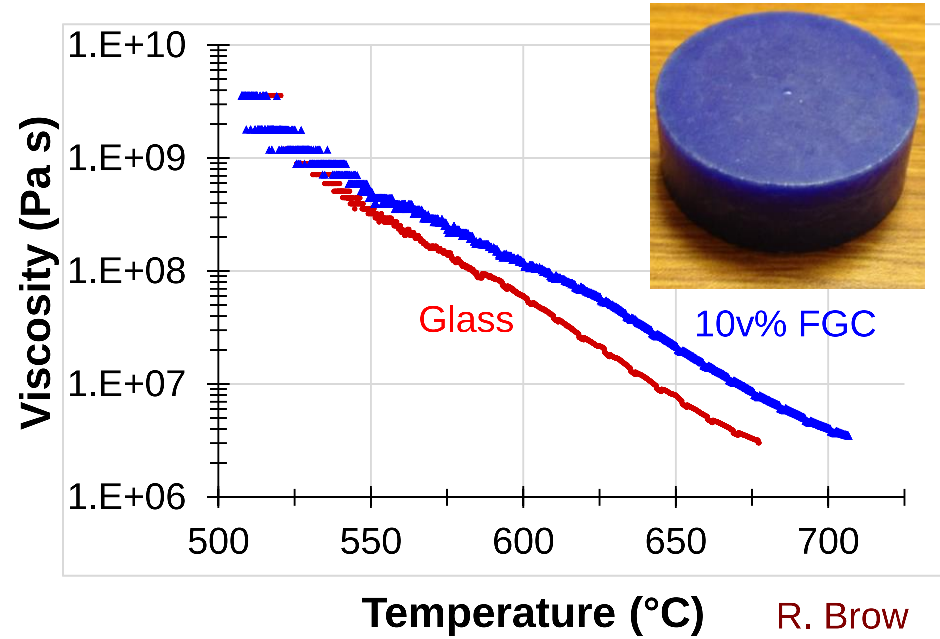




T. Zeitler

Filled-Glass Composite (FGC) Properties Are Consistent With Model Predicted Trends





R. Brow
MO U S&T

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

Euler's Model

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

Viscosity Data Will Enable The Use Of Process Modeling To Optimize FGC Designs For Manufacturability

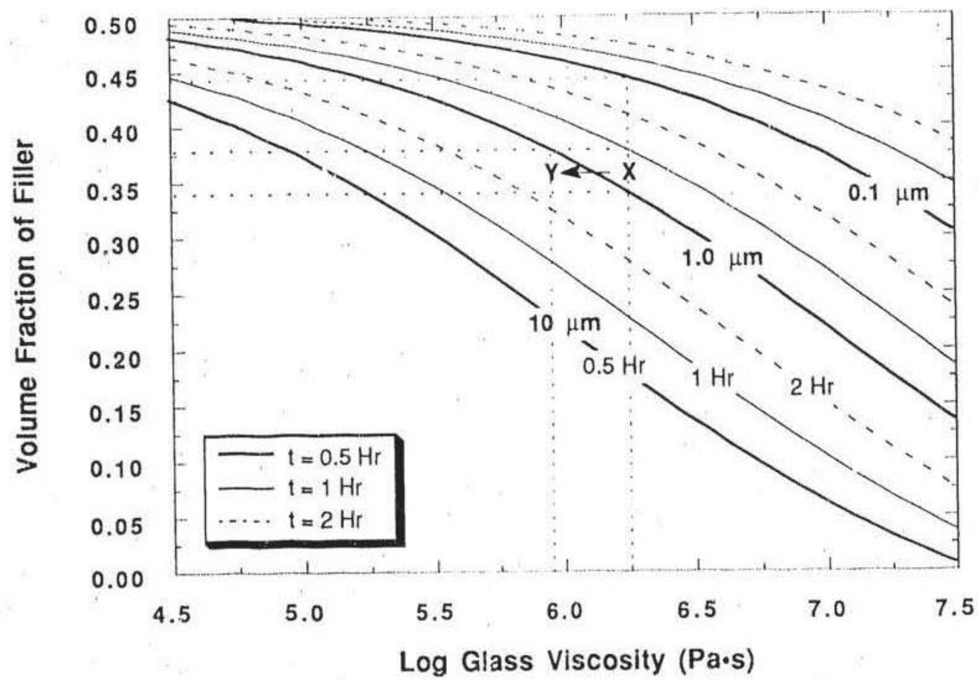
Euler's Model

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

NLPS Model

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

FGC Process Map



Ewsuk & Harrison, Ceramic Trans, 1995

Sessile Drop Experiments Were Completed On Stainless Steel To Characterize Wetting & Viscous Flow

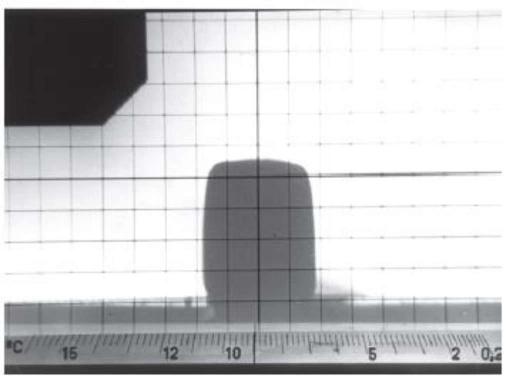
Sandia National Laboratories

R. Brow – MO U S&T

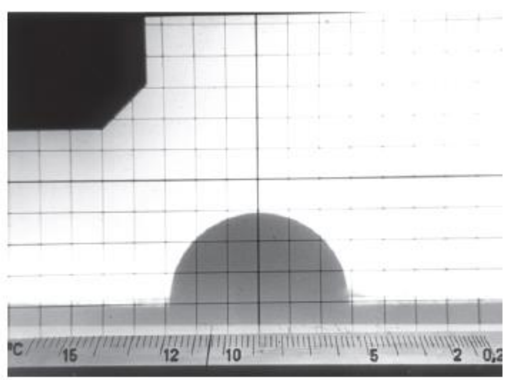
Sessile Drop Data Were Analyzed To Better Quantify Differences In Viscous Behavior

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).

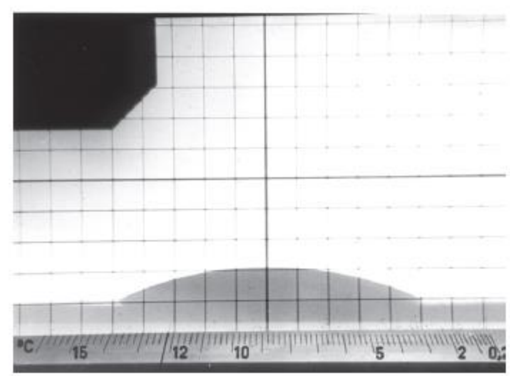
Scholze, "Influence of viscosity and surface tension on hot-stage microscopy measurements on glasses," *Ver. Dtsch. Keram. Ges*., 1962, **391**, 63–8.)



Softening Point



Half Ball Point

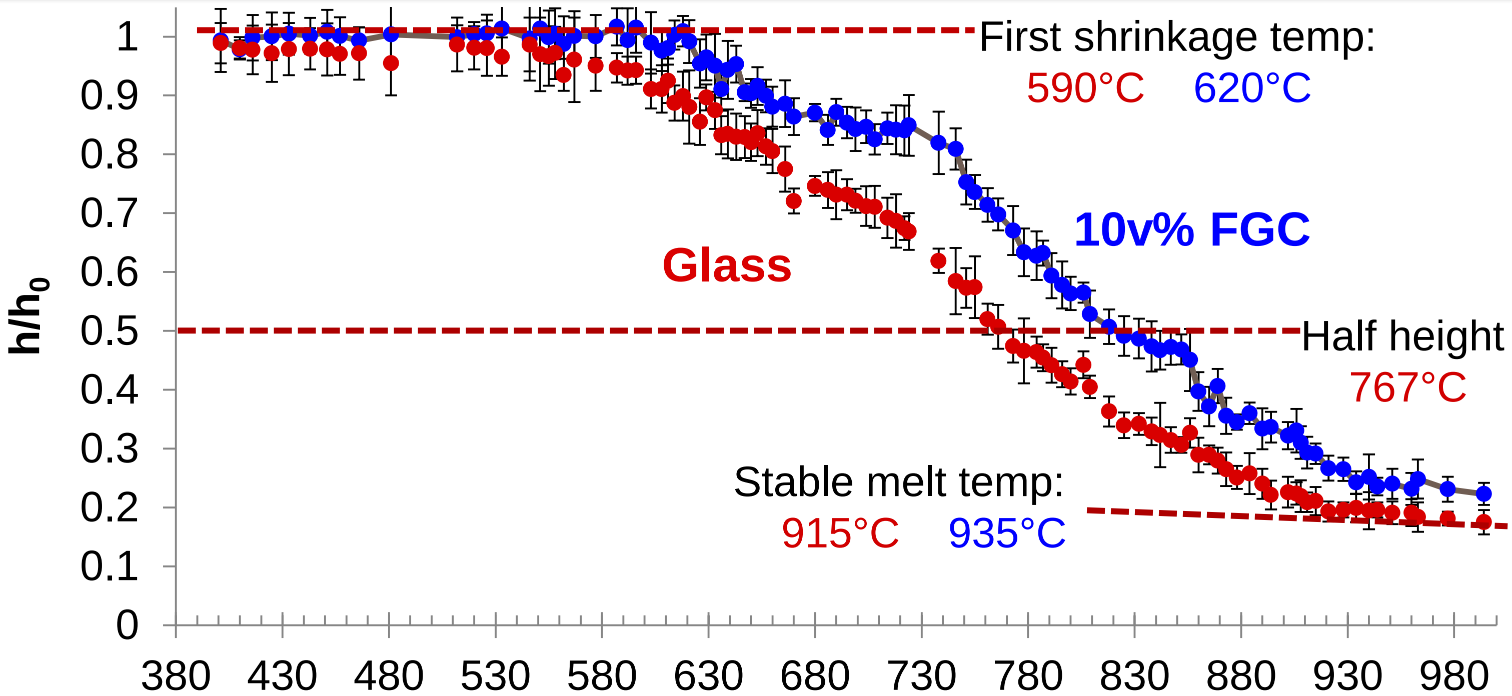


Flow Point

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

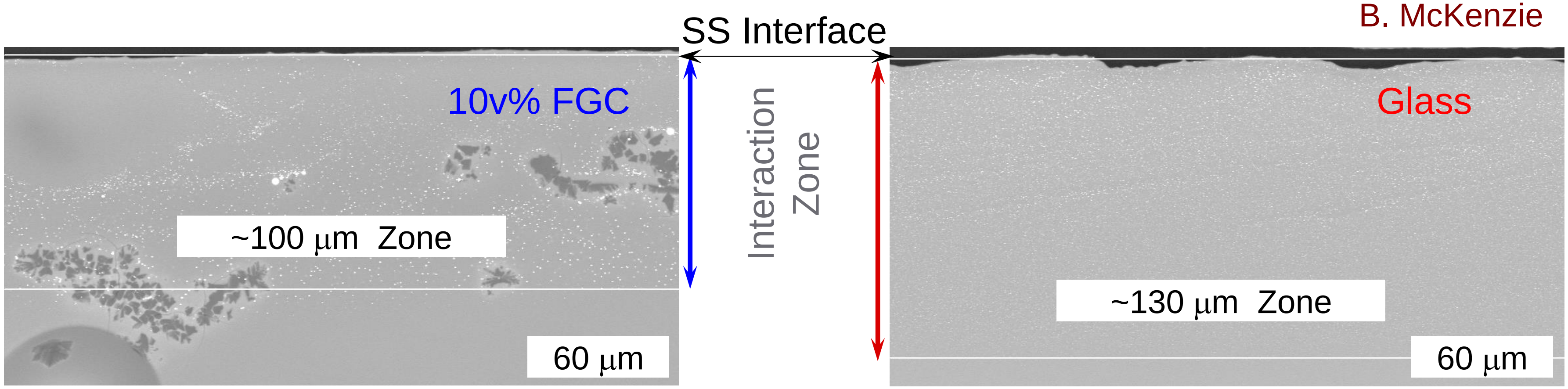
The Filler Addition Increases FGC Viscosity And Decrease FGC Reactivity Relative To The Glass

Sandia National Laboratories



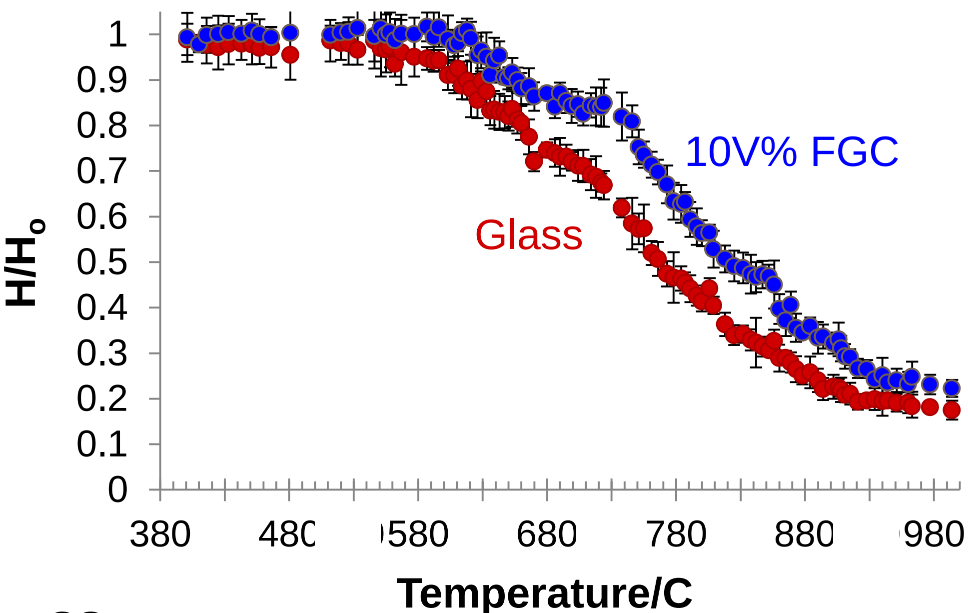
R. Brow
MO U S&T

B. McKenzie

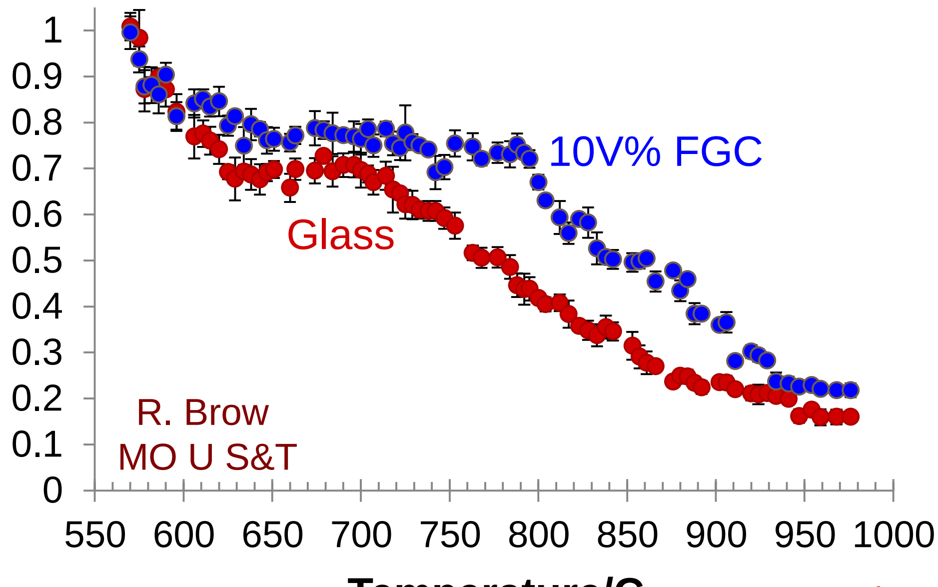


Oxidizing The Stainless Steel Enhances Initial Wetting And Reaction

Wetting on SS

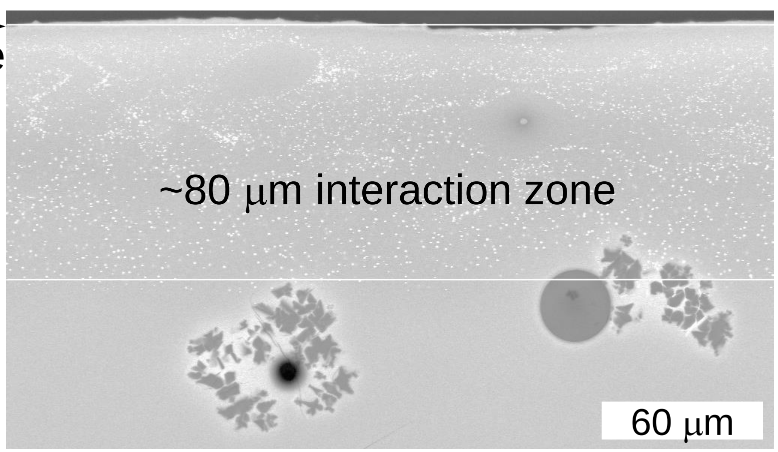


Wetting on Oxidized SS

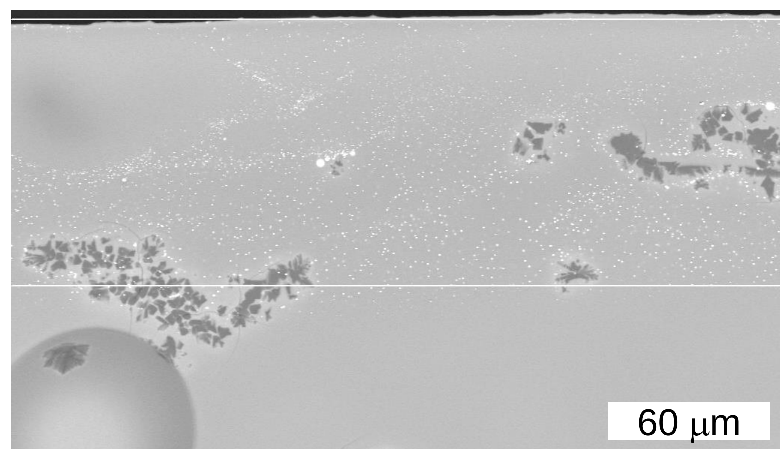


B. McKenzie

SS Interface



FGC composite



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

Summary

- Characterized & Modeled Glass Chemistry-Structure.
  - Good modelling-experiment first-order agreement.
    - MD efficient to assess bulk glass chemistry-structure.
  - Interface modeling consistent with expectations
    - Higher surface concentration of network modifiers.
- Characterized & Modeled FGC Properties & Processing.

  Measured CTE & viscosity trend as predicted by modeling.
  - Wetting & reactivity are consistent with expectations
    - Higher viscosity & lower reactivity FGCs relative to glass.
    - Initial wetting & reactivity are enhanced on oxidized SS.