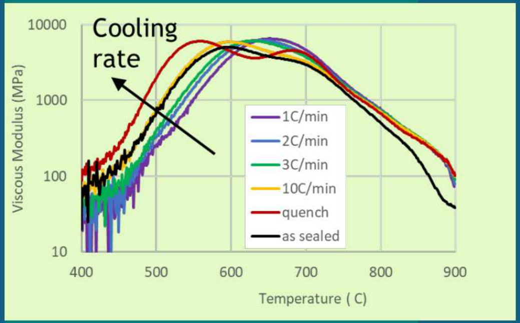
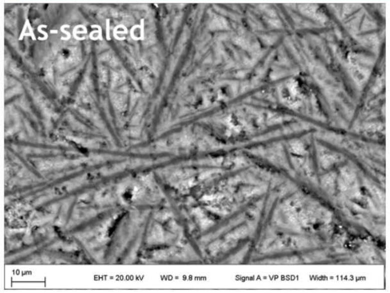
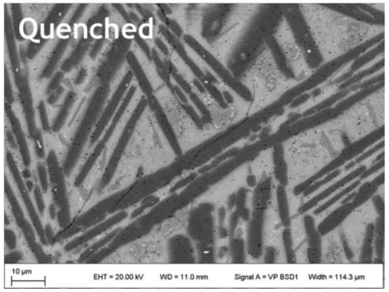
Sandia National Laboratories

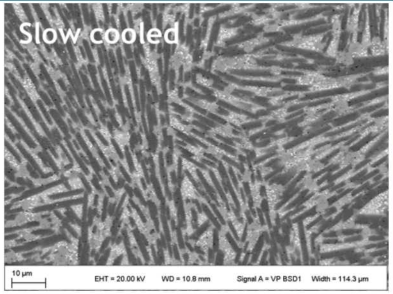
SAND2019-12716C

Rheology of glass-ceramics for sealing applications









PRESENTED BY

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Outline

- Introduction to glass and glass ceramic to metal seals
- Modeling needs
- Measurement of shear moduli
- Construction of master curve and calculation of activation energy
- Thermal dependence of microstructure
- Conclusions

What is a hermetic connector?

Barrier to gas/liquid transfer between environments.

- Allow electrical transmission

Designed for extreme conditions

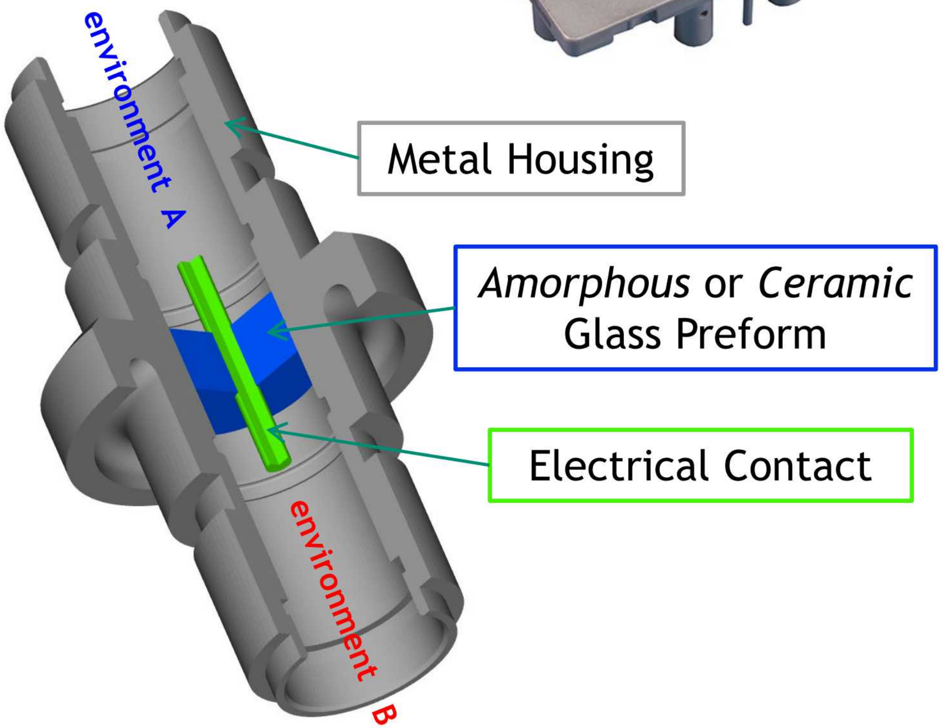
- Thermal
- Pressure
- Shock/vibration

Many applications:

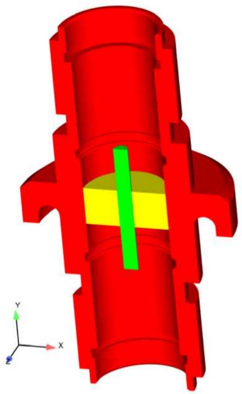
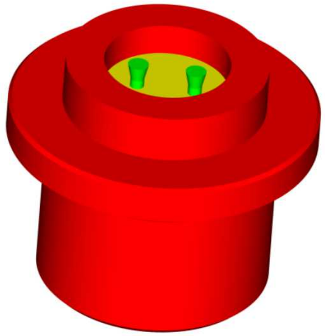
- Satellites, submarine vehicles, medical, telecommunications, etc.

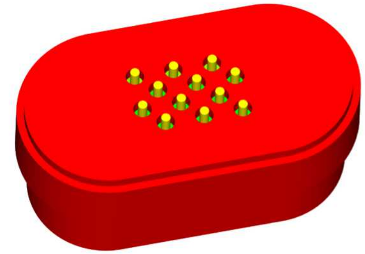
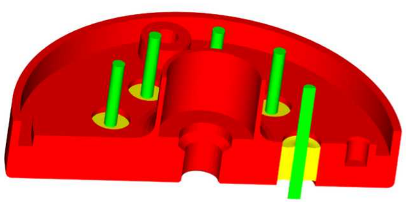
Types of hermetic connectors

- Matched seals
- **Compression seals**

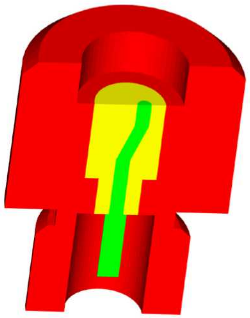
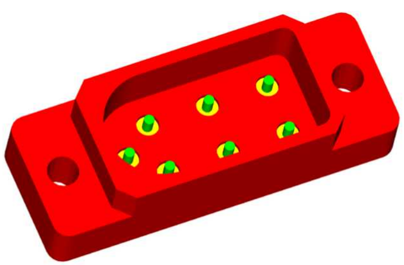


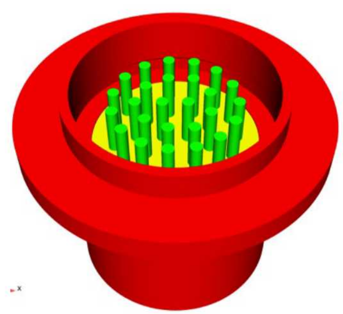
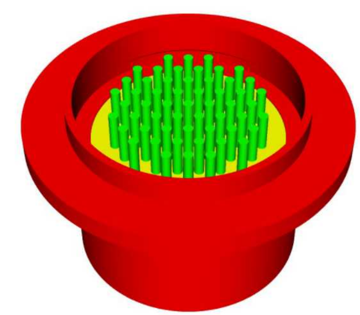
Glass to Metal Seal designs have evolved over the years

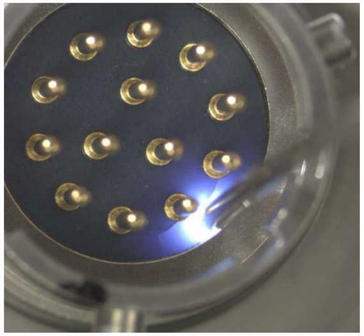



- increasingly complex geometries
- more pins & tighter spacing
- extended life-time requirements
- more complicated materials (e.g., glass ceramics)

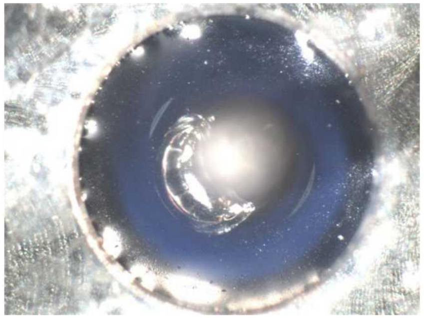



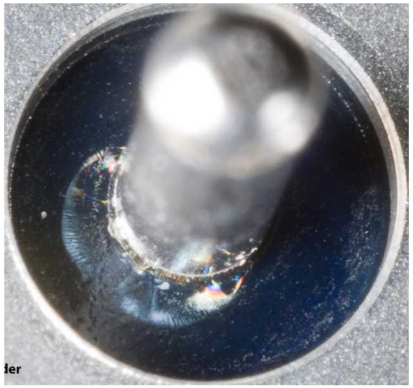
And yet, despite years of experience . . . .
. . . We still are asking the same questions



How to design a robust seal?
- Will part remain hermetic?
- Meet life-time requirements?
- Re-use?

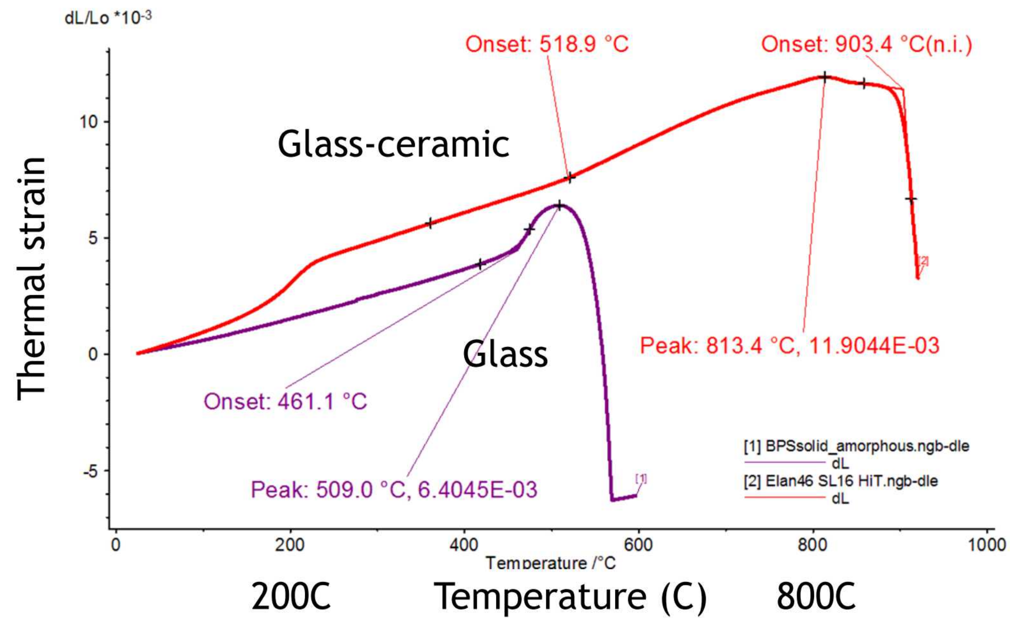
Why did the glass crack?
- still hermetic? remain so?
- foreign debris (glass chips)?
- pin stability – short circuits?
- accept or reject parts?



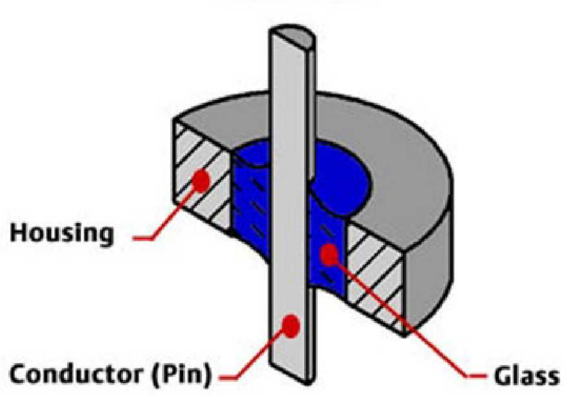


Why Glass-Ceramic to Metal seals?

- Process/reflow like glasses
- High temp stability after crystallization
  - Abnormal high T/P environment
- High coefficient of thermal expansion (CTE)
  - Most sealing glasses < 12 ppm/°C
- Crystallization → tunable coefficient of thermal expansion
- Matched seals:
  - CTE Glass ceramic ≤ CTE housing
- Composite microstructure → toughness/strength



Material	CTE (ppm/°C) (40 -600°C)
304L SS shell	18.89
Glass Ceramic*	16-17
Paliney7 pin	15.76



Sandia Patented Glass Ceramic

Oxide	Wt%
SiO_2	74.3%
B_2O_3	1.2%
Li_2O	12.7%
Al_2O_3	3.8%
K_2O	2.9%
P_2O_5	3.1%
KnO	1.8%

Glass network former (SiO_2, B_2O_3)

Glass network modifier (Li_2O, Al_2O_3)

P_2O_5 → Li_3PO_4 nuclei for crystallization

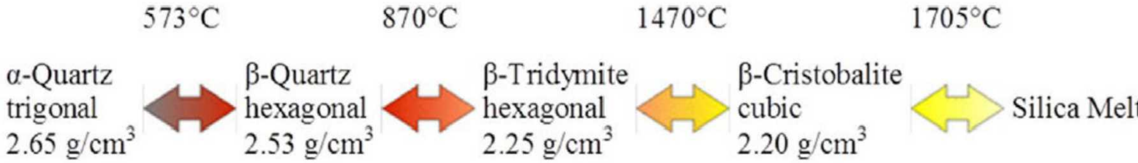
KnO → Corrosion resistance

Phase	CTE (ppm/°C, 40–600°C)
SiO_2, glass	0.5
SiO_2, Quartz	23.3
SiO_2, Cristobalite	27.1
Li_2SiO_3	13.0 (20-300°C)
$Li_2Si_2O_5$	11.0

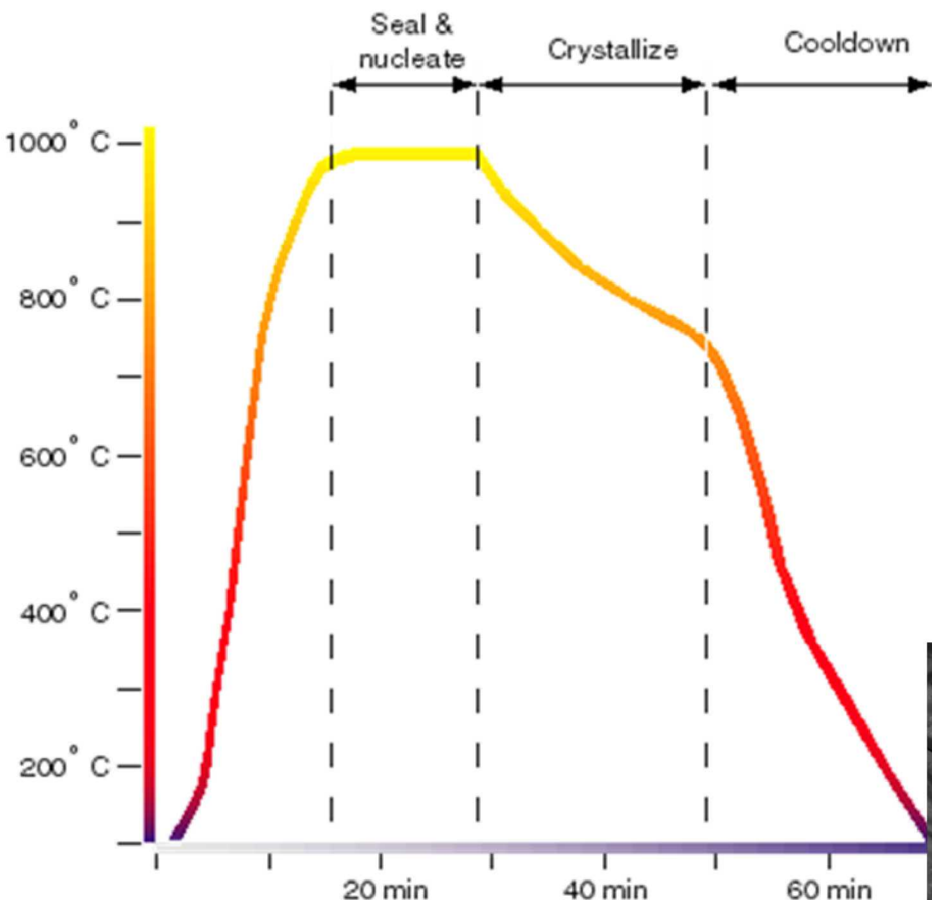
More cristobalite ↓ Higher CTE

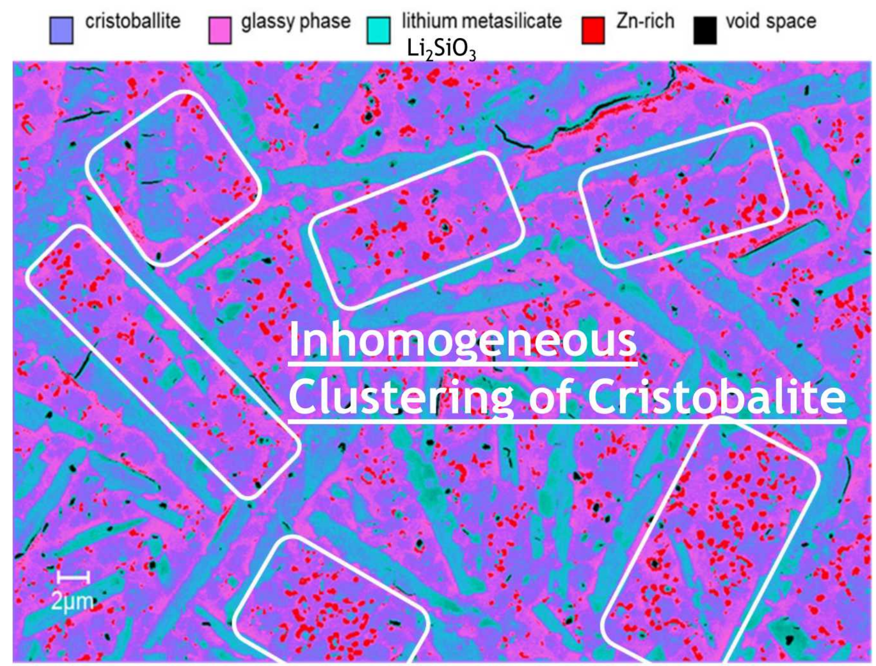
Dai et al. (2016) J. Am Ceramic Soc

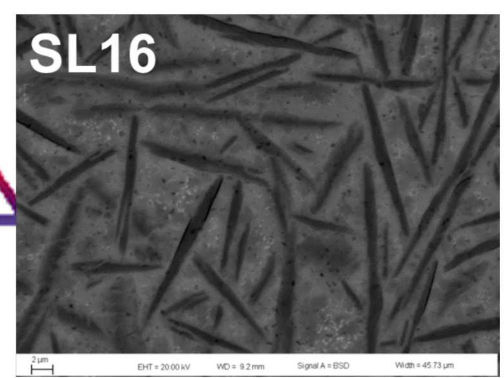
Sandia SL16 Glass-ceramics, process and microstructure

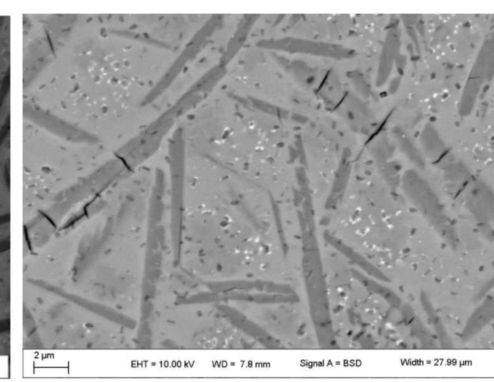


As sealed thermal profile





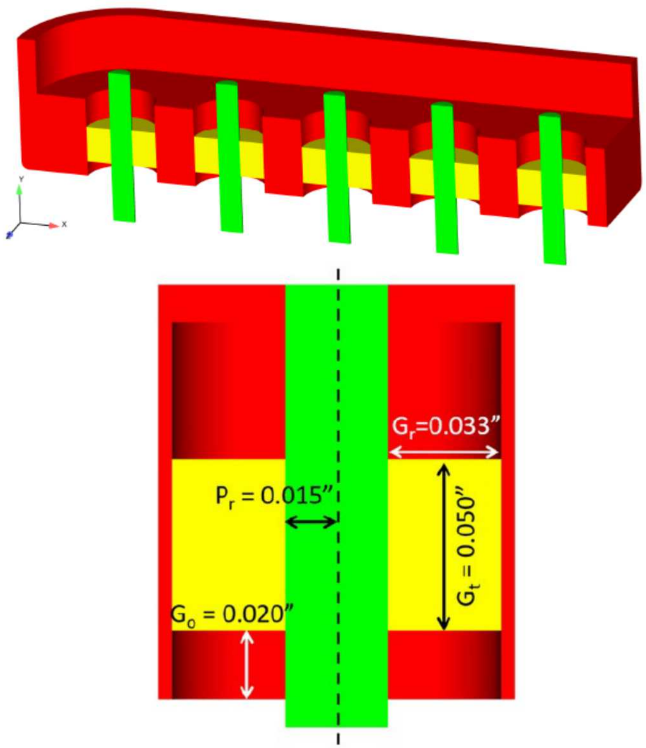


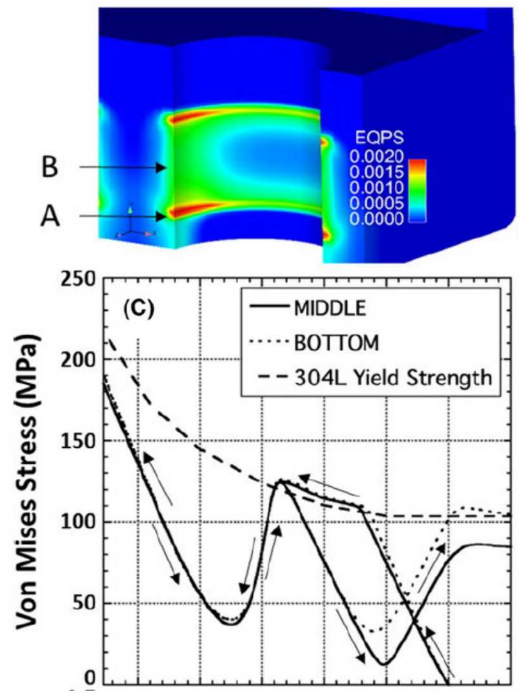


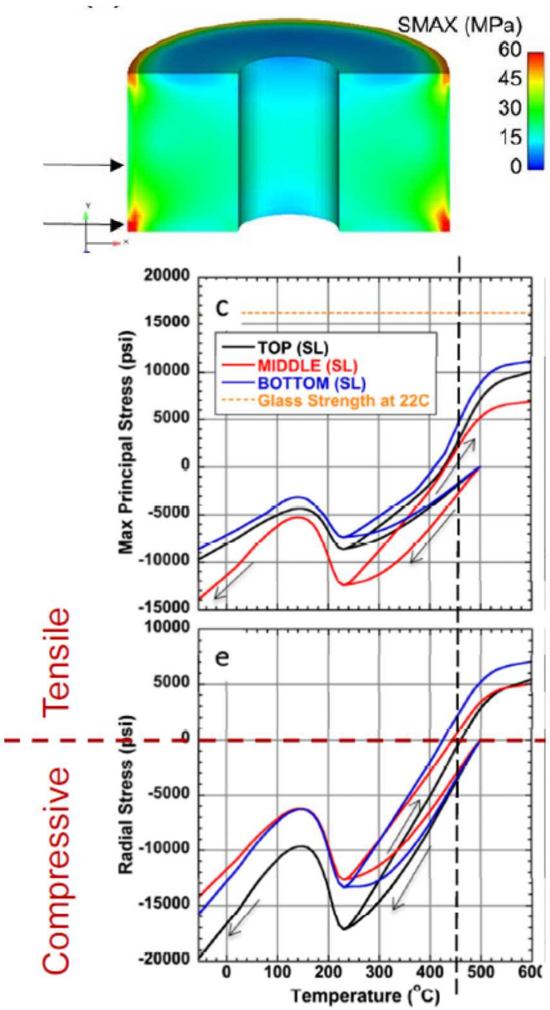
Dai et al. (2016) J. Am Ceramic Soc

Thermal Stress and Strain Prediction

Use Sierra codes to predict stresses and strains after seal processing







Current predictions are limited to extrapolation of materials properties from 600°C

Dai et al. (2017) J. Am. Ceramic Soc.

Anton Paar:CTD1000 Rheology capability

Rectangular torsion geometry measures shear moduli
Fixtures are made of inconel and they are the only standard ones rated to 1000°C
The stainless steel torsion fixtures are not rated above 600C due to warping
The CTE mismatch doesn’t seem to be causing a problem though some slipping with low CTE glasses

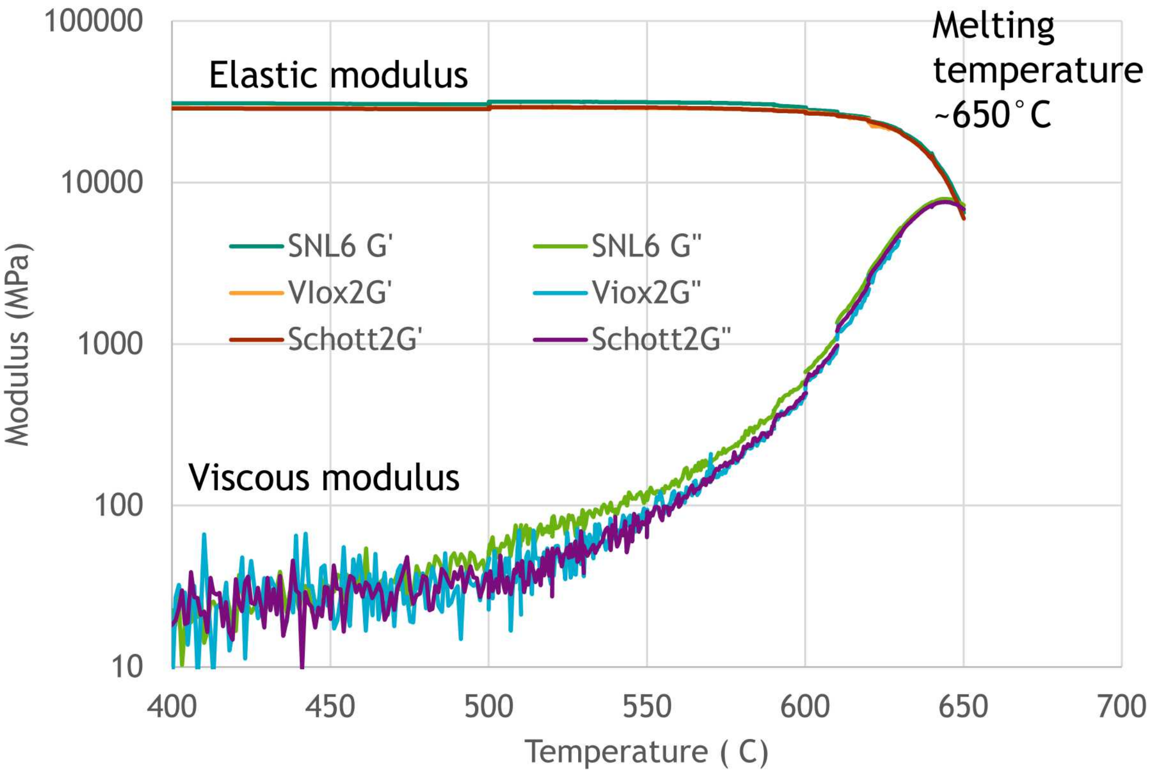
Specifications: sample SRF	
Width of sample	1 mm to 12 mm
Thickness of sample	1 mm to 12 mm
Length of sample	**max. 40 mm**

Glass Moduli Temperature Dependence

CABAL 12 is a traditional sealing glass $20MgO\text{-}20CaO\text{-}20Al_2O_3\text{-}40B_2O_3$

Silica free glass developed for lithium battery applications

Comparison of three manufacturer lots



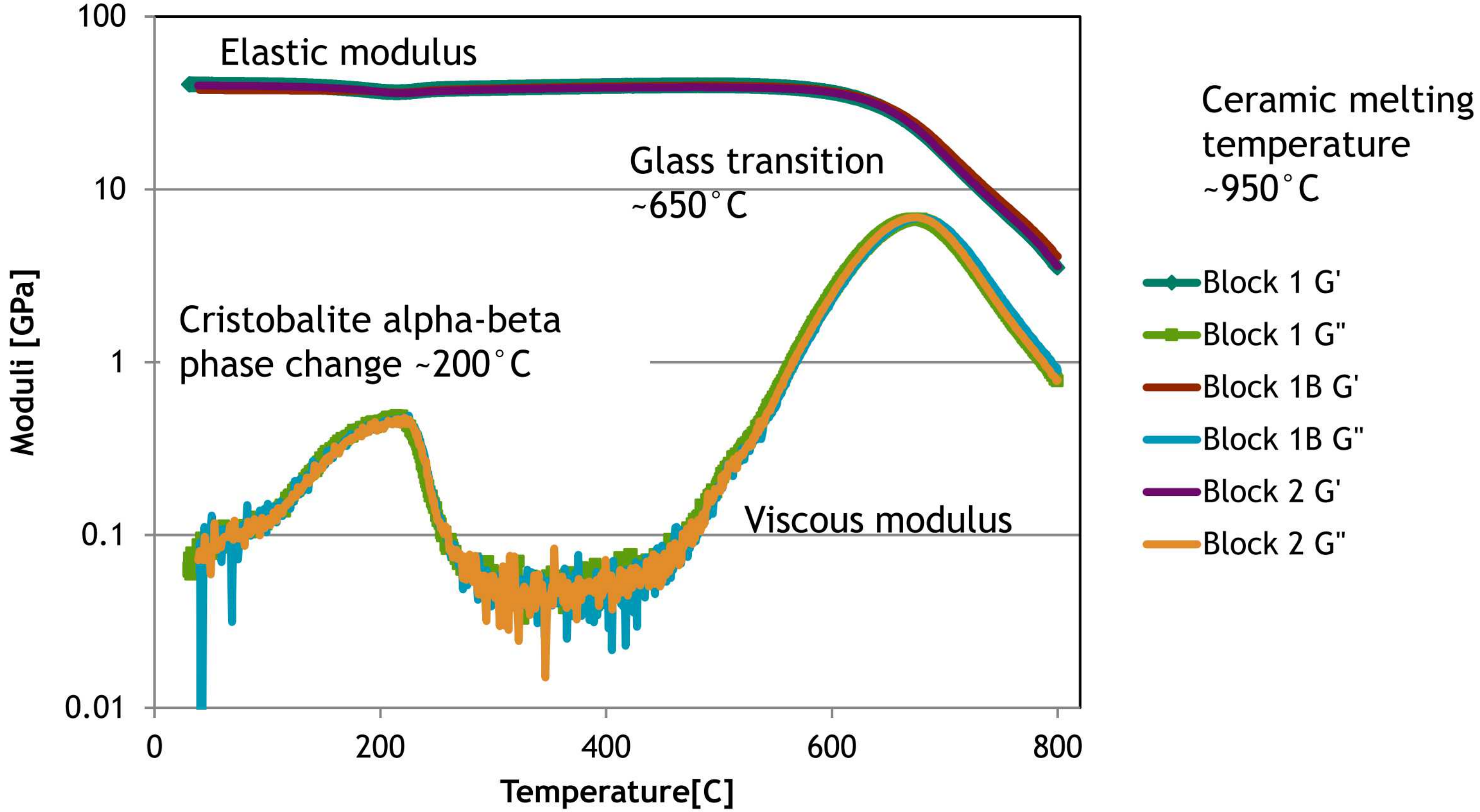
1 Hz, 0.001% strain

Glass-Ceramic Moduli Thermal Dependence

SL 17 composition is Li_2O-SiO_2-Al_2O_3-K_2O-B_2O_3-P_2O_5-ZnO, Ceramed

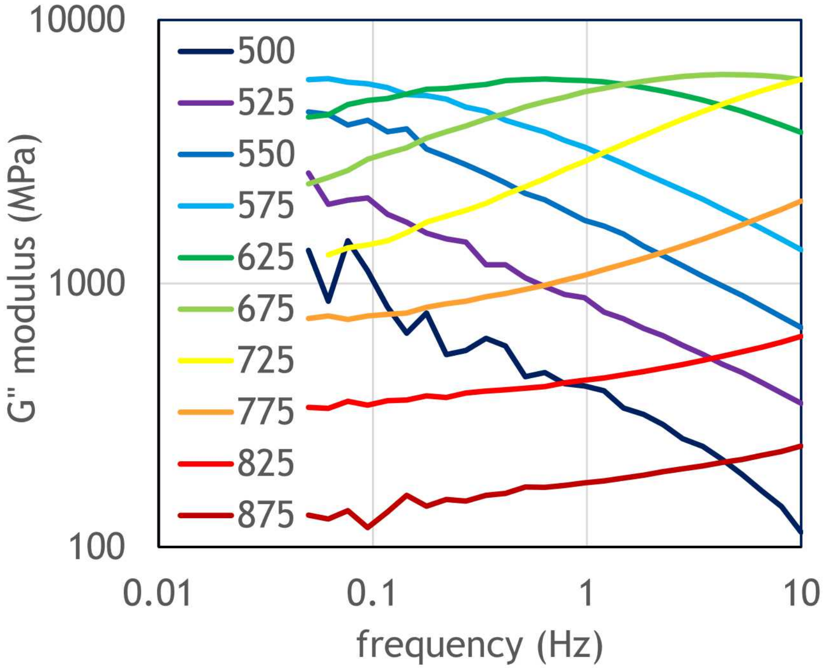
Annealed 6 /16/16 – 5˚C/min to 700, hold 30min, 1˚C/min to RT

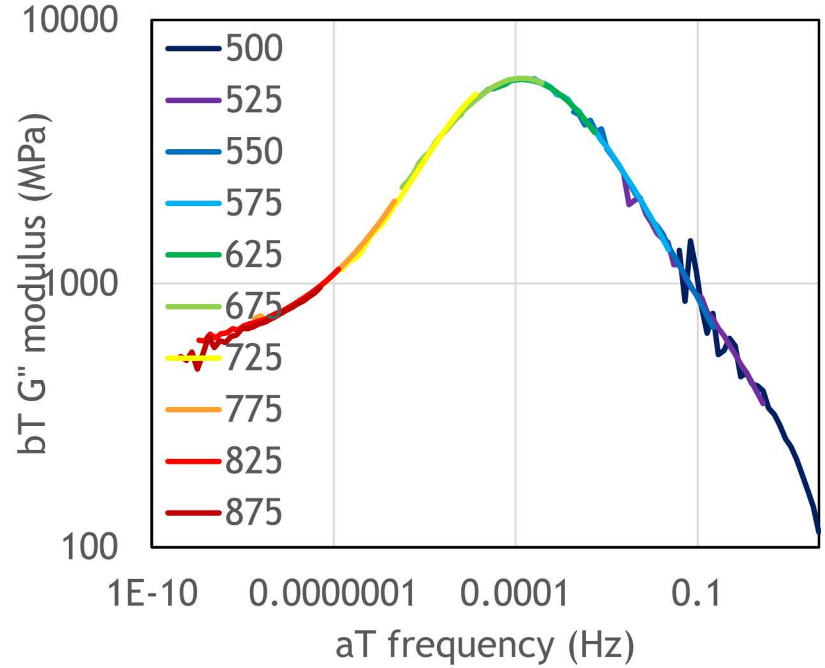
SL derived from step like change in thermal strain caused by cristobalite phase change. 17 refers to CTE ~ 17 ppm/ºC



1 Hz, 0.001% strain

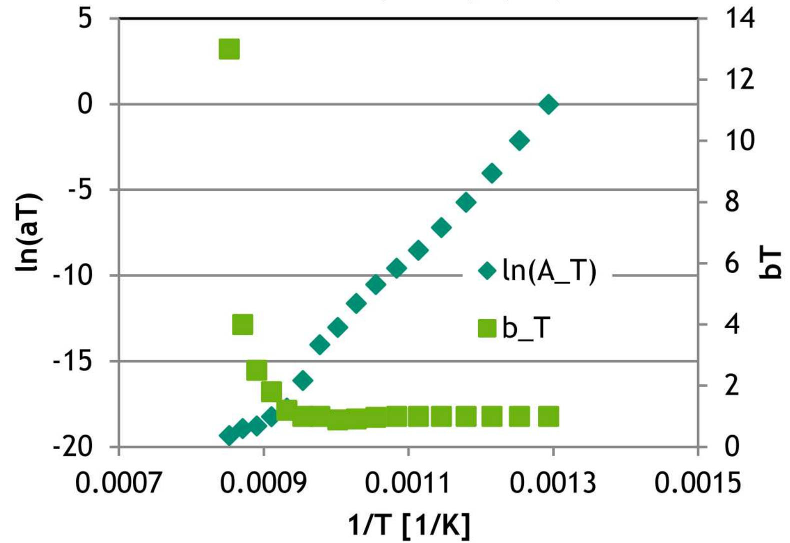
Construction of a Master Curve





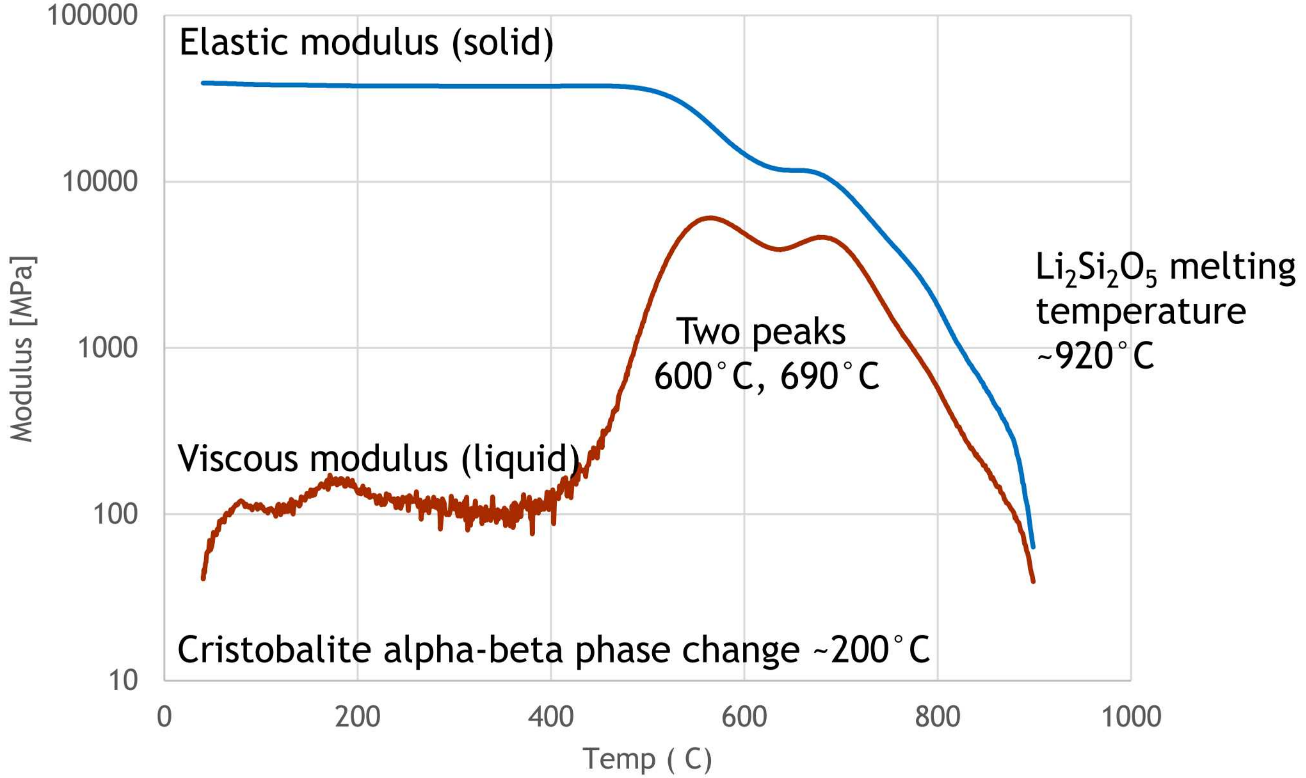
Frequency dependence of viscous modulus as a function of temperature

Apply time temperature superposition to develop a master curve and calculate Arrhenius activation energy



Glass-Ceramic Thermal Dependence

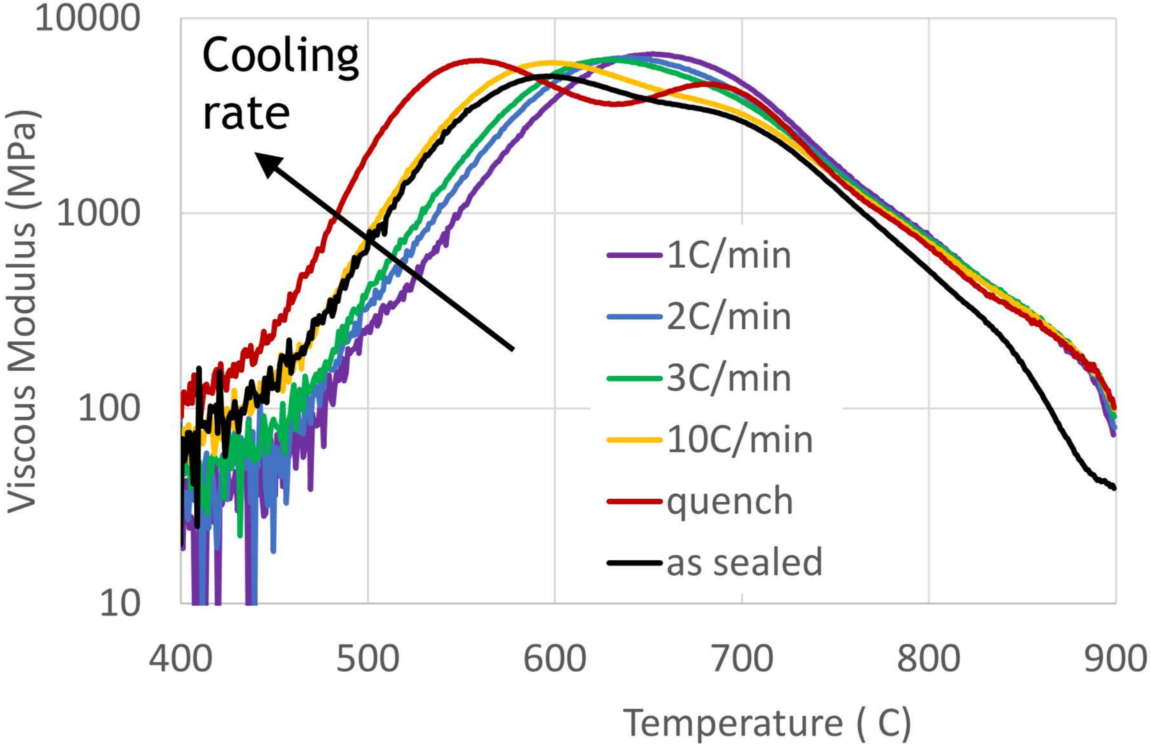
SL16 was ceramed from the same parent crystallizable glass using a different thermal processing, with less high expansion Cristobalite phase, and thus lower CTE ~ 16 ppm/ºC.



1 Hz, 0.001% strain

Temperature Dependent

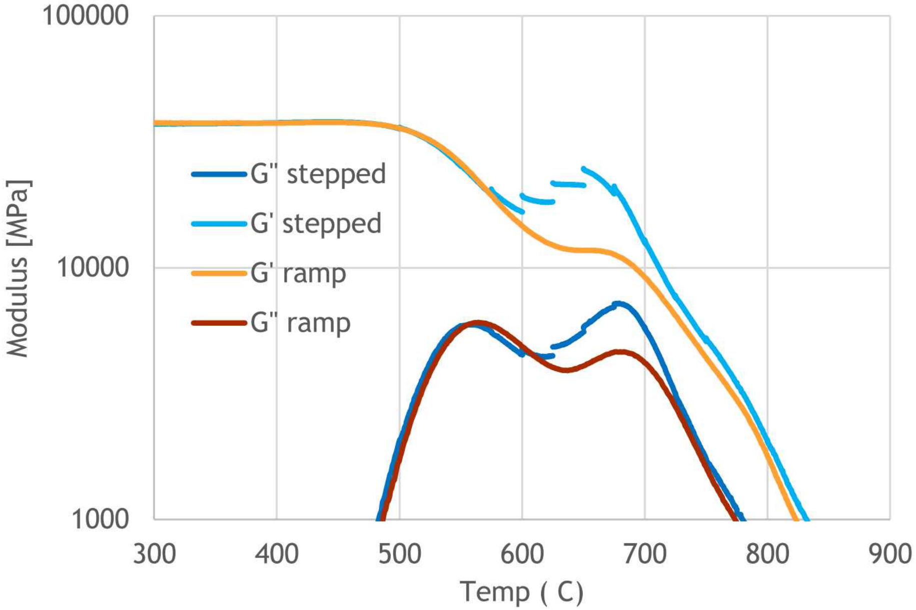
See strong dependence in glass transition *during heating* by vary cooling rate from 1°C/min to quenched (decrease ~400°C /10 min)

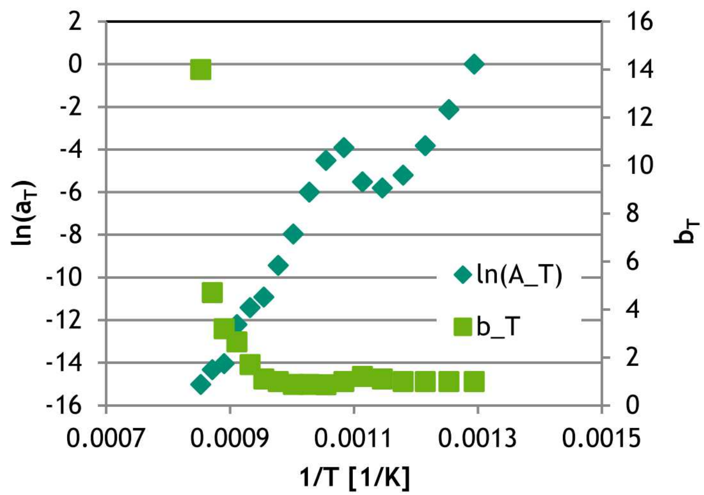


Dynamic restructuring in SL glass ceramics

Time temperature superposition shows evidence of dynamic restructuring of the glass-ceramic well below the melting temperature

Time temperature superposition shows two distinct Arrhenius activation energies,
- Relaxation of residual glass (<600ºC activation energy
- "Re-arrangement" of the crystalline phase, or "configurational" relaxation
- Previous studies found the crystalline composition was stable up to 650ºC





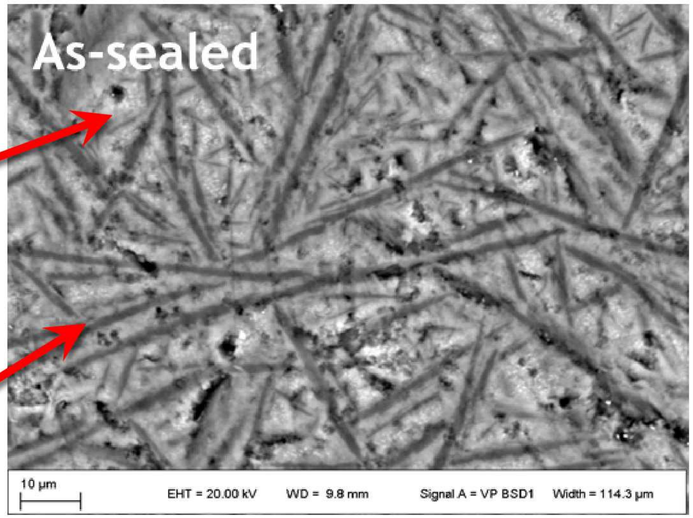
Rodriguez et al. (2016) J. Am Ceram. Soc.

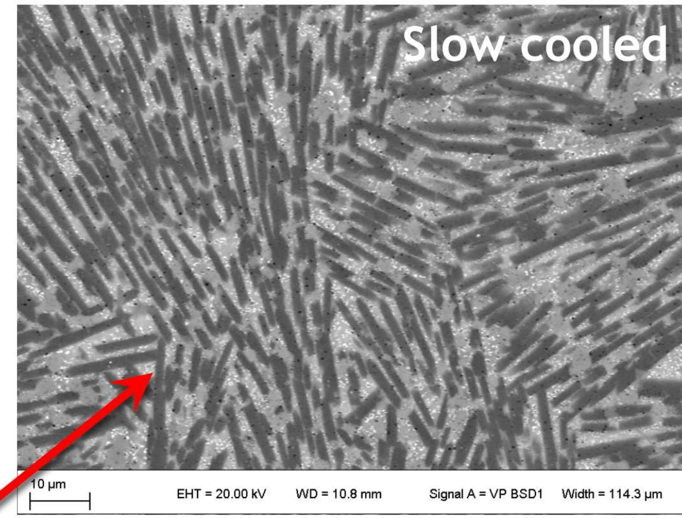
Temperature Dependent Microstructure

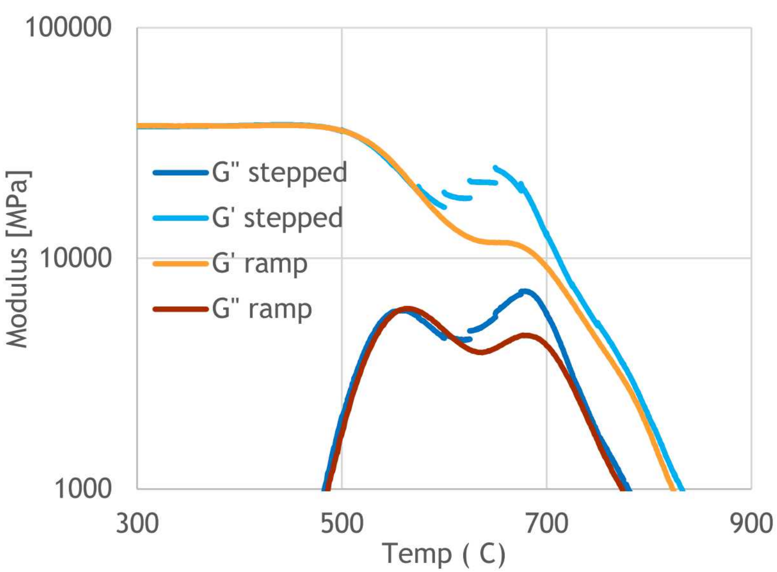
Rearrangement is believed to be controlled by diffusion through viscous glassy phase

SiO_{2CR}

Li_2SiO_3

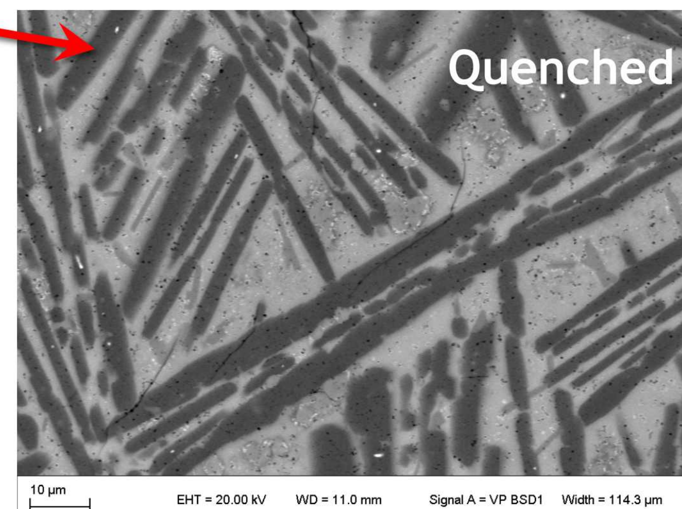




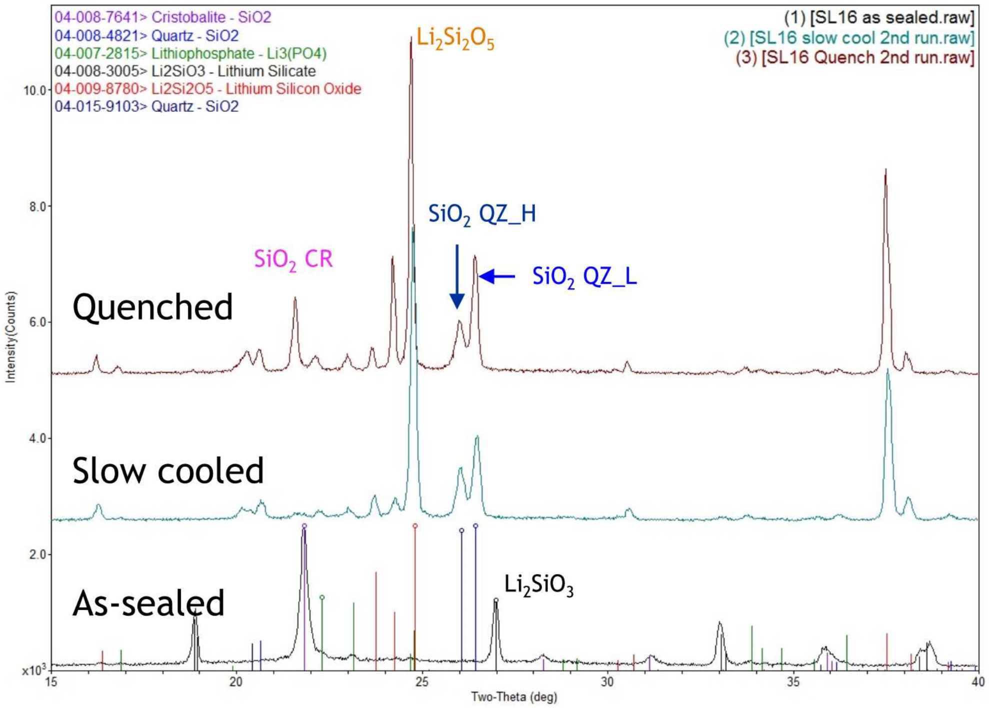


$Li_2Si_2O_5$

Melts ~



XRD of Crystalline Phases



As-sealed

Phase	SL16
	wt%
Quartz Low SiO_2	2.51
Cristobalite SiO_2	24.37
Li_2SiO_3	36.82
Li_3PO_4	7.94
Amorphous	28.36

Quenched

Complete transition
$Li_2SiO_3 + SiO_{2CR} \rightarrow Li_2Si_2O_5$

Partial transition
$SiO_{2CR} \rightarrow SiO_{2QZ\_low} + SiO_{2QZ\_high}$

Slow cooled

Complete transition
$Li_2SiO_3 + SiO_{2CR} \rightarrow Li_2Si_2O_5$

$SiO_{2CR} \rightarrow SiO_{2QZ\_low} + SiO_{2QZ\_high}$

Cooling from 900 ºC, the crystalline phases of glass-ceramics changed from the original as-sealed state

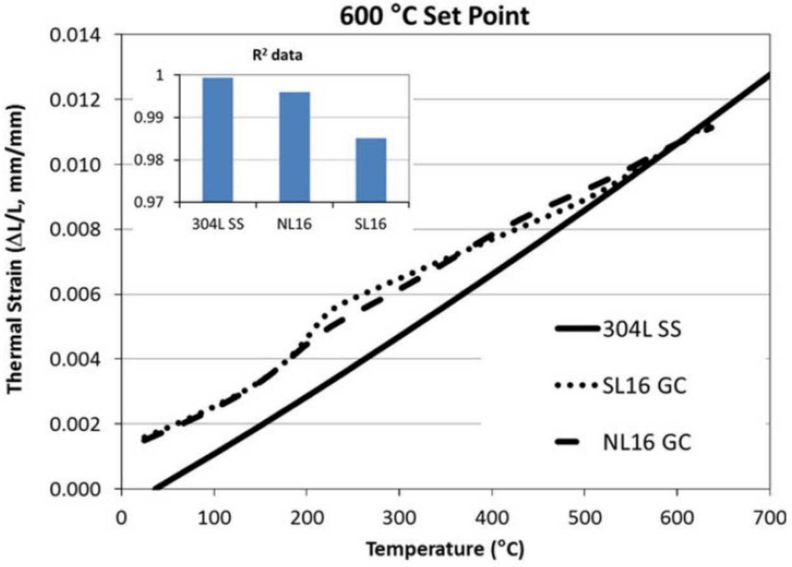
The phase conversion also depended on the cooling rate

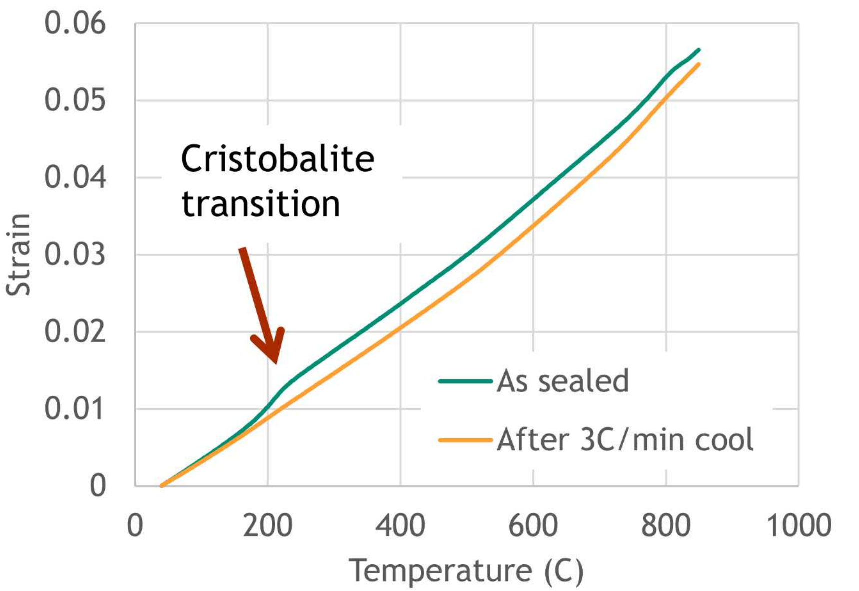
Phase conversion likely dominated by bulk diffusion processes in a “viscous” glassy state above glass transition temperature

Thermal Strain Measurement

Rheometers aren't designed to measure thermal expansion coefficients, but they capture the qualitative trends and are able to access a wider range of temperatures

- Magnitude of thermal strain is wrong, perhaps due to inappropriate thermal gap correction calibration.





Conclusions

Able to measure shear moduli of glass and glass ceramic sealing materials through their glass transition temperature up to edge of melting transition (-60-950°C)

- Cristobalite alpha-beta phase transition
- Glass transition of material or glassy matrix

Time Temperature Superposition can generate a shear modulus master curve

More complex for glass-ceramics

- Slow-cooled: Acting like a glass with single Arrhenius activation energy related to the glass relaxation
- Quenched: Two distinct Arrhenius activation energies,
  - low temperature dynamics match the relaxation of slow cooled – due to melting of the glassy phase
  - higher temperature dynamics related to the "re-arrangement" of the crystalline phase, or "configurational" relaxation

Extra slides