Viscous Glass/Composite SOFC Sealants

Scott Misture, James Shelby, co-PIs
Mark Naylor, graduate student

NYS College of Ceramics at Alfred University
Alfred, NY

DOE Project Manager: Dr. Joseph M. Stoffa

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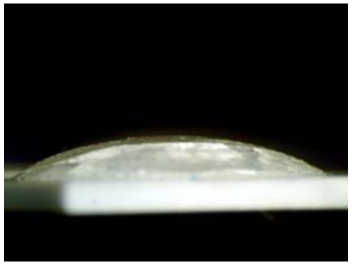
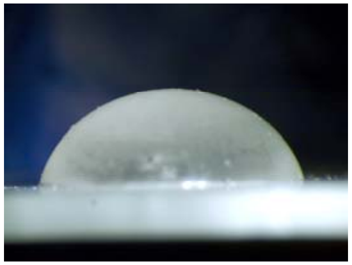
Significant Results: Identified Two Novel Glass Systems for Viscous Seals

Several new Ga silicate, Ge silicate and B-Ge silicate glasses display promising properties:

- Viscosities of 10^3 (viscosity of cold honey) to 10^6 Pa·s (just softening) at 850°C
- Limited crystallization in bulk and powder form, with Ga playing a major role in inhibiting crystallization
- Weight losses of <0.25 wt.% after 504 hours at 850°C
- CTE values between 8 and 11 ppm/K (100 – 400°C)

All with < 10 mol% B_2O_3 and <10mol% alkali oxides





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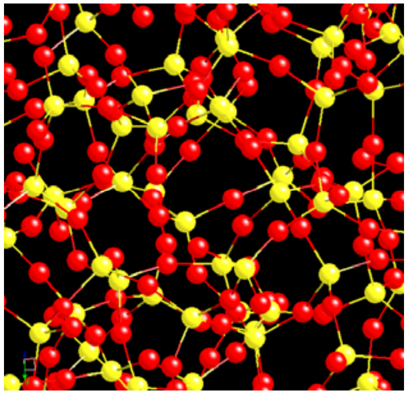
Overall Strategies for Viscous Sealants

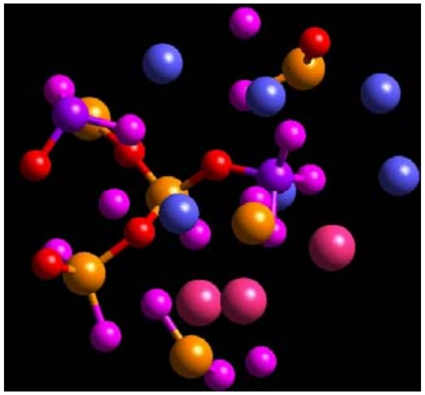
- Fully amorphous
  No crystallization on heating or cooling

- Fully amorphous at operating temperature
  Any crystals formed on cooling melt during heating

- Partially amorphous at operating temperature
  Remnant amorphous phase has correct viscosity and volume fraction to allow flow even with crystals present



All network formers = very little flexibility



Modified network = enormous flexibility

Initial Search for Appropriate Glass Compositions

CTE values near 10 – 12 ppm/K
Alkali content 20 mol% or lower

High Temperature Glasses

High SiO_2 content
590 < Tg < 770°C
-Flow at 850°C ranges from roofing cement to barely softening

Primary parameters to optimize:

- Viscosity
- Alkali content
- Crystallization

Low Temperature Glasses

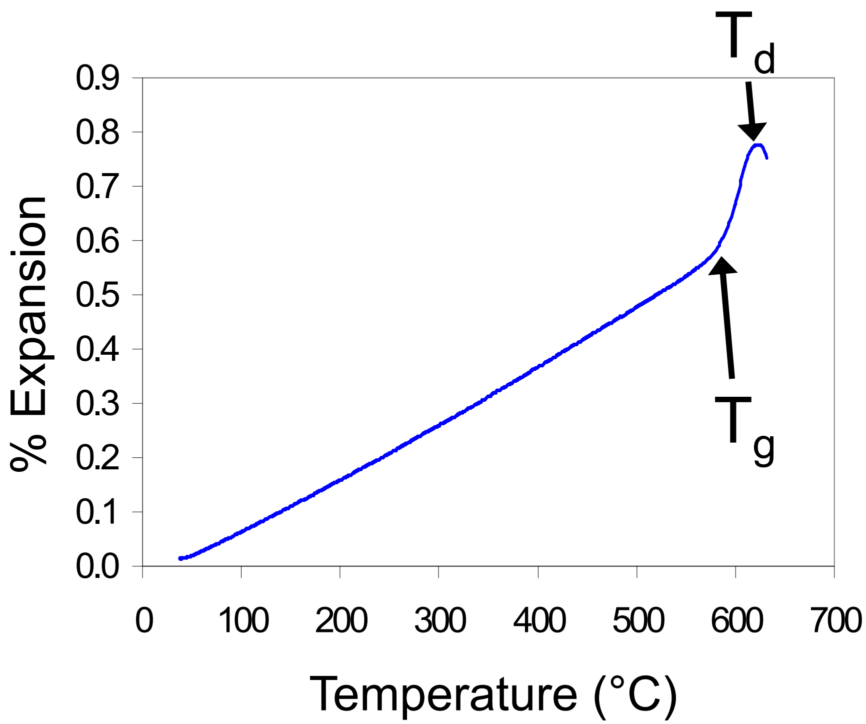
High GeO_2, B_2O_3, or P_2O_5 content
514 < Tg < 590°C
-excellent flow < 850°C

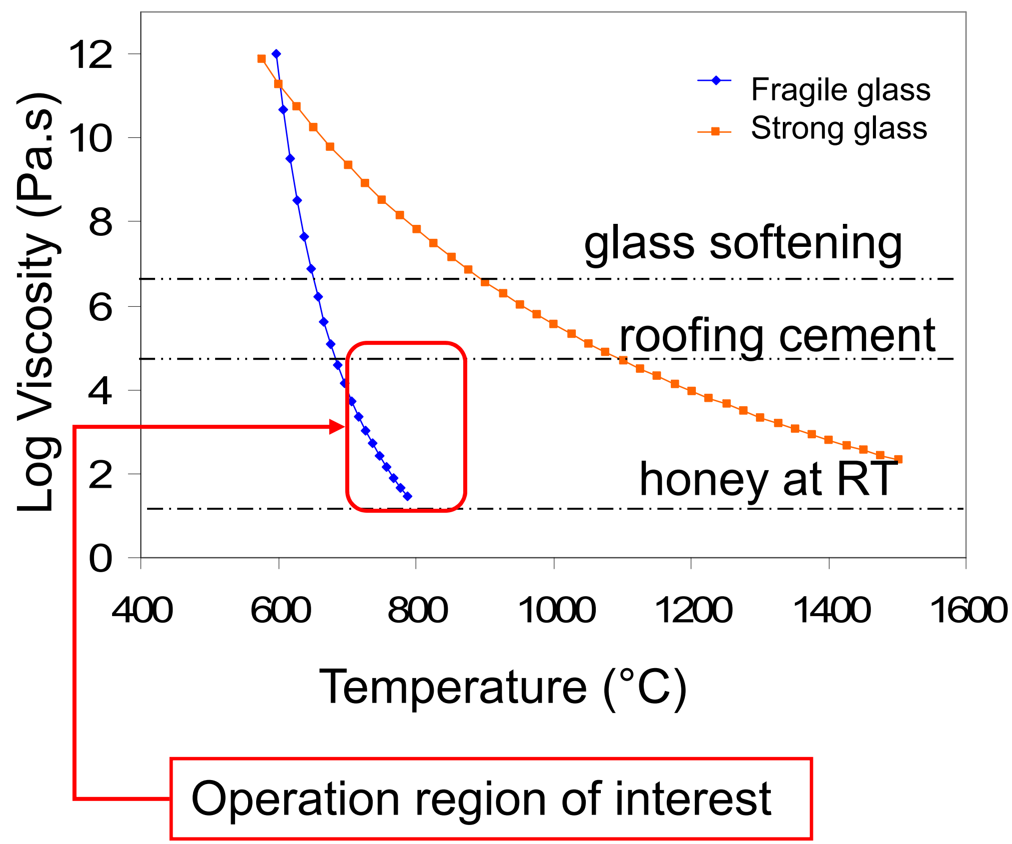
Primary parameters to optimize:

- Volatility
- Alkali content
- Crystallization

Study both in parallel paths

Screening glass properties – softening and viscosity





Viscosity estimated from simple DSC analysis for screening

Optimization of high Tg, high viscosity silicates

Initial Silicate Glasses
CTE 10-12 ppm/K, 20 mol% alkali

→ Ga_2O_3 substitutions

resists crystallization, lower Tg: 590–640°C

→ Substitute SrO, ZnO for alkali, SiO_2

increase Tg, decrease η

→ Substitute B_2O_3 for alkali

decrease Tg and η

→ Fine compositional modification

(future work) additions of WO_3, F^-, GeO_2, mixed alkaline earths, La_2O_3, Y_2O_3, Ta_2O_3

Glasses with large degree of crystallization, no flow by 900°C

Chemical Substitutions to Reduce Tg and Td

Entirely New Glass Compositional Series

- Use of Ga_2O_3 instead of Al_2O_3
  - Ga ions lower Tg compared to identical Al containing glasses
- Use of GeO_2 for SiO_2: GeO_2 exhibits properties similar to B_2O_3
  - high CTE, lower Tm than SiO_2, greater chemical durability than borate glasses
  - allows lower Tg
  - May form Ge colloids in the fuel atmosphere (inhibit with B_2O_3)
- Use combined Ga_2O_3 or GeO_2 with B_2O_3
  - Lower viscosity with lower alkali

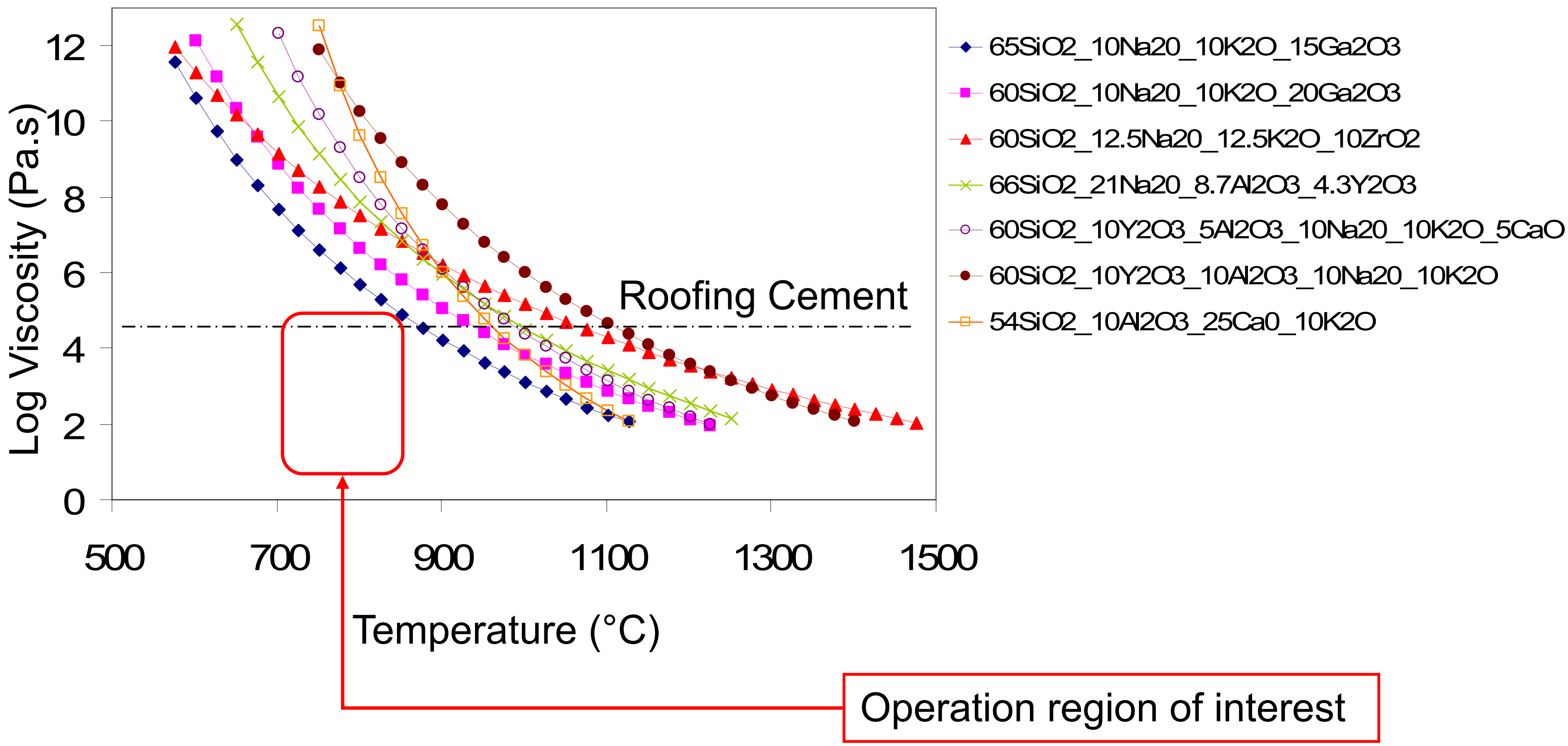
In all cases consider alkaline earths and Zn to reduce alkali

Initial High Temperature Silicates – with 600 < Tg < 700°C

Composition (mole %)	CTE 100-400 °C (ppm/K)	Tg (°C)	T_d (°C)	viscosity during melting
$54SiO_2$_$10Al_2O_3$_25CaO_$10K_2O$	9.74	770	~824	Easily poured
$60SiO_2$_$20Ga_2O_3$_$10Na_2O$_$10K_2O$	11.76	**640**	712	Flows, can not pour
$60SiO_2$_$10Y_2O_3$_$5Al_2O_3$_5CaO_$10Na_2O$_$10K_2O$	10.47	725	755	Can be poured
$60SiO_2$_$10Y_2O_3$_$10Al_2O_3$_$10Na_2O$_$10K_2O$	10.23	760	~830	Easily poured
$62SiO_2$_$8Al_2O_3$_21CaO_$8K_2O$	8.87	750	828	Easily poured
$66SiO_2$_$4Y_2O_3$_$8Al_2O_3$_$21Na_2O$	9.98	**671**	725	Easily poured
$66SiO_2$_$10Y_2O_3$_$23Na_2O$	10.49	**679**	724	Easily stirred
$65SiO_2$_$15Ga_2O_3$_$10Na_2O$_$10K_2O$	11.79	**594**	615	Flows, can not pour

Note effect of Ga in lowering Tg

Ga Silicates Approach the Operating Window for Flow Behavior



Behavior over 500 hours

Bulk specimens heat treated at 850°C for 504 hours in air

Composition (mole %)	**Crystallization Amount**	**% Wt Loss**
$65SiO_2\_15Ga_2O_3\_10Na_2O\_10K_2O$	**Very minimal**	**0.19**
$60SiO_2\_10Y_2O_3\_5Al_2O_3\_5CaO\_10Na_2O\_10K_2O$	Complete	0.99
$60SiO_2\_4.3Y_2O_3\_8.7Al_2O_3\_21Na_2O$	Mostly	0.14
$60SiO_2\_20Ga_2O_3\_10Na_2O\_10K_2O$	**Very minimal**	**0.23**
$60SiO_2\_15Ga_2O_3\_25K_2O$	Mostly	---
$58.5SiO_2\_11Nb_2O_5\_19.5BaO\_11K_2O$	Complete	---
$65SiO_2\_15ZrO\_12.5Na_2O\_12.5K_2O$	Complete	---
$60SiO_2\_10Y_2O_3\_10Al_2O_3\_10Na_2O\_10K_2O$	Complete	0.45
$54.5SiO_2\_10Al_2O_3\_25CaO\_10.5K_2O$	Complete	0.38
$60SiO_2\_10Y_2O_3\_23Na_2O$	Mostly	0.14
$62SiO_2\_8Al_2O_3\_21CaO\_8K_2O$	Complete	0.05

500 hours for powders – to measure worst-case crystallization

Powdered specimens heat treated at 850°C for 504 hours in air

Composition (mole %)	Crystallization	Flow behavior
65SiO_2_15Ga_2O_3_10Na_2O_10K_2O	Very minimal	Moderate
60SiO_2_20Ga_2O_3_10Na_2O_10K_2O	Minimal	Poor
60SiO_2_15Ga_2O_3_25K_2O	Minimal	Poor
60SiO_2_10Y_2O_3_5Al_2O_3_5CaO_ 10Na_2O_10K_2O	Complete	None
60SiO_2_4Y_2O_3_8Al_2O_3_21Na_2O	Mostly	Moderate

Weight loss below 0.4 % in all cases

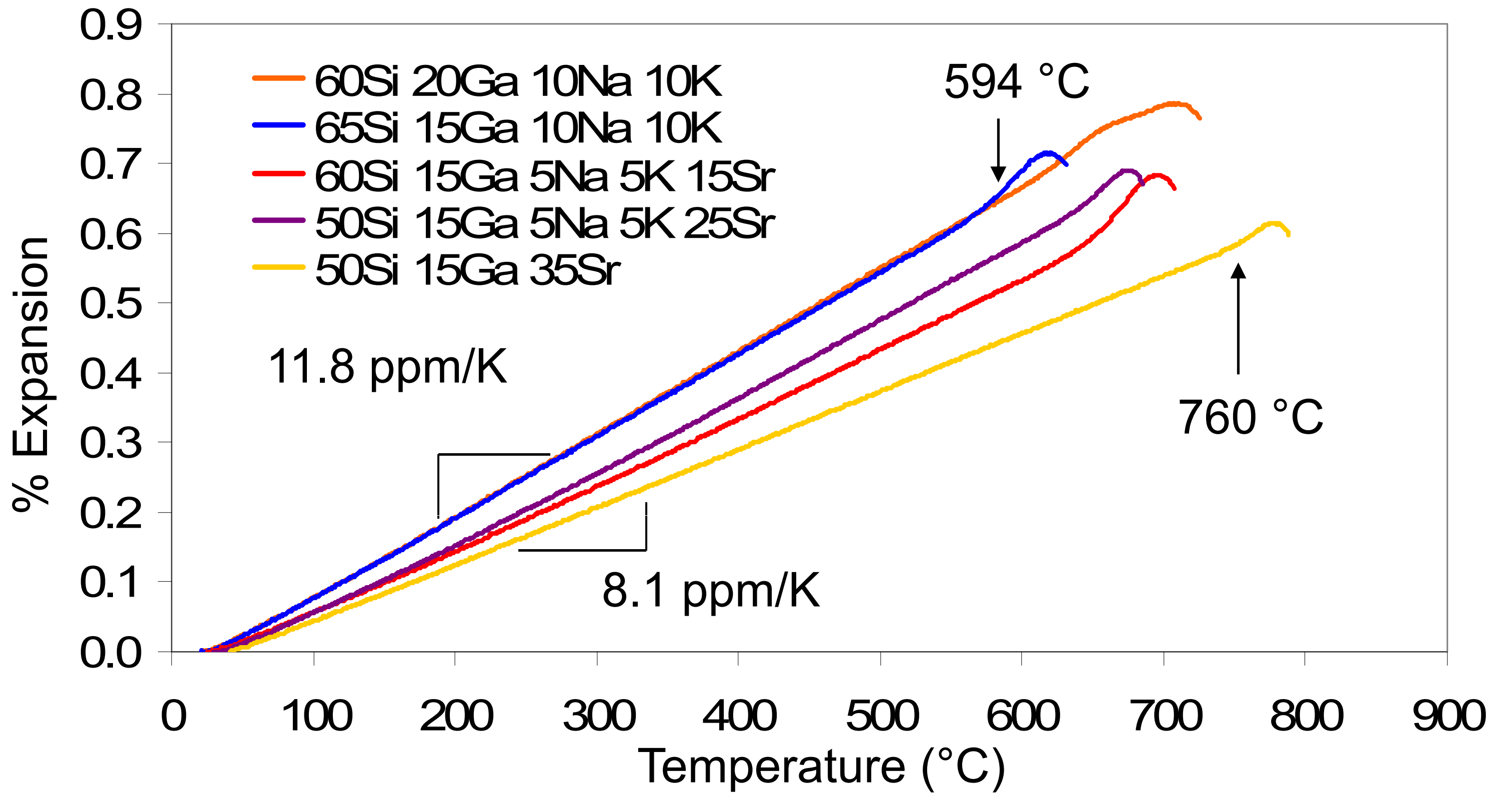
500 hours for powders – to measure worst-case crystallization

Powdered specimens heat treated at 850°C for 504 hours in air

Composition (mole %)	Flow behavior
$65SiO_2\_15Ga_2O_3\_10Na_2O\_10K_2O$	Moderate
$60SiO_2\_20Ga_2O_3\_10Na_2O\_10K_2O$	Poor
$60SiO_2\_15Ga_2O_3\_25K_2O$	Poor
$60SiO_2\_10Y_2O_3\_5Al_2O_3\_5CaO\_10Na_2O\_10K_2O$	None
$60SiO_2\_4Y_2O_3\_8Al_2O_3\_21Na_2O$	Moderate

Weight loss below 0.4 % in all cases

Downselect to Galliosilicates & Re-Optimize: *Success in Reducing Tg by up to 50°C*



500 hour cycles and additional characterization is underway

Optimization of low Tg, low viscosity silicates

Initial Low Tg Glasses

GeO_2, Ga_2O_3 SiO_2, P_2O_5 glasses

Low Tg: 492 – 626°C

GeO_2 - SiO_2

Excellent flow behavior, low Tg, no crystallization BUT risk of forming Ge colloids in H_2 atmosphere

B_2O_3 additions

stabilizes Ge ions into four-fold coordination

Substitute SrO, ZnO for alkali

Results in extensive crystallization

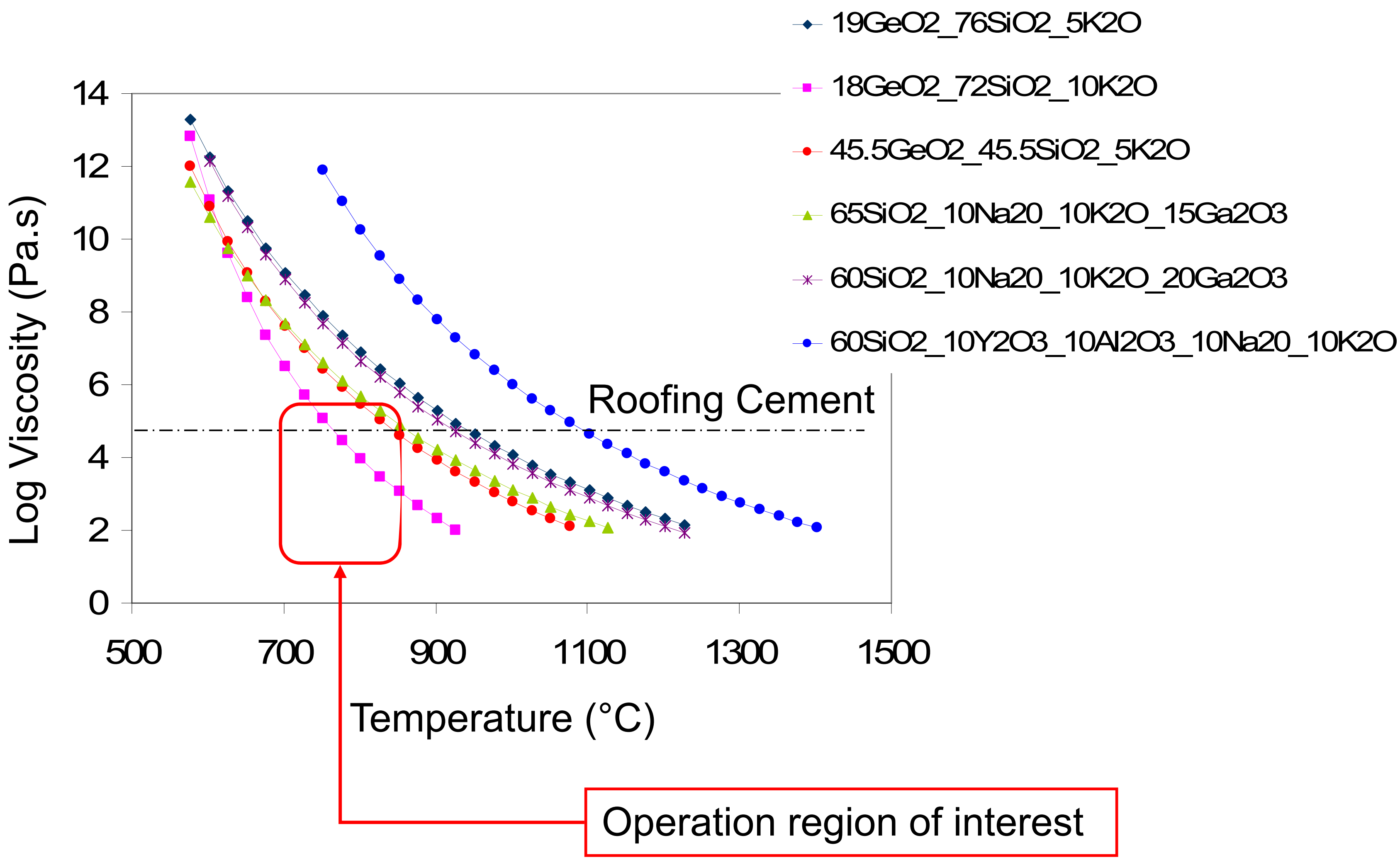
Additions of Ga_2O_3

improves glass formation

Ba-Na-P_2O_5

Excellent flow, but extreme volatility at 850°C

Some New Germanosilicate Glasses Meet Approximate Viscosity Specification



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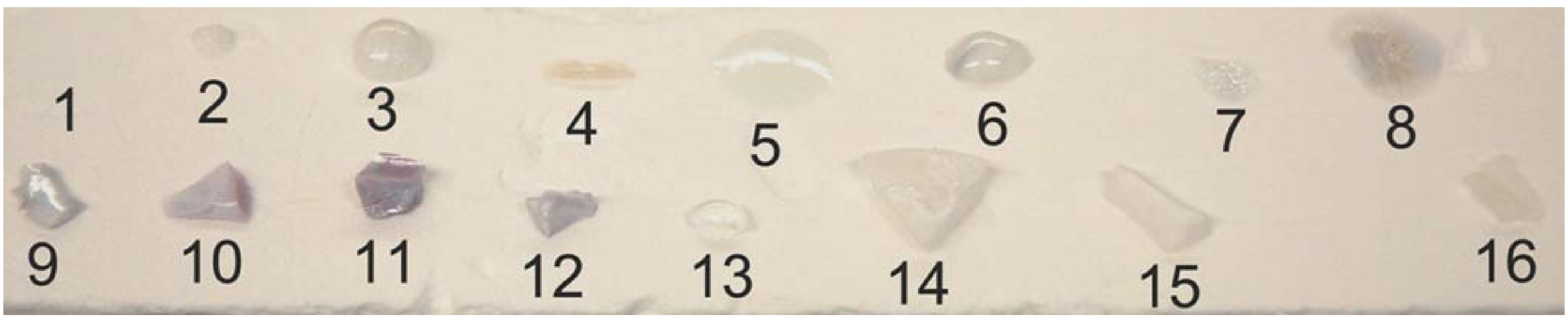
Germanosilicate flow test – 12 h at 850°C

#	Composition	Flow behavior
1	$50P_2O_5\_40BaO\_10Na_2O$	Complete evaporation
2	$19GeO_2\_76SiO_2\_5K_2O$	Fused/slumped
3	$18GeO_2\_72SiO_2\_10K_2O$	Fused/slumped
4	$68GeO_2\_17SiO_2\_15K_2O$	Fused/slumped
5	$17GeO_2\_68SiO_2\_15K_2O$	Flowed
6	$47.5GeO_2\_47.5SiO_2\_5K_2O$	Flowed
7	$45GeO_2\_45SiO_2\_10K_2O$	Flowed
8	$42.5GeO_2\_42.5SiO_2\_15K_2O$	Flowed

#	Composition	Bonding
9	$80GeO_2\_8CaO\_12Na_2O$	No fusing or slumping
10	$80GeO_2\_4CaO\_16Na_2O$	No fusing or slumping
11	$80GeO_2\_10CaO\_10Na_2O$	No fusing or slumping
12	$75GeO_2\_12.5CaO\_12.5Na_2O$	No fusing or slumping
13	$90GeO_2\_5Al_2O_3\_5K_2O$	Flowed
14	$80GeO_2\_10Al_2O_3\_10K_2O$	Fused/no slumping
15	$90GeO_2\_5Al_2O_3\_5Na_2O$	Fused/some slumping
16	$70GeO_2\_15Al_2O_3\_15Na_2O$	Not fused



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500 hour behavior promising

Powdered specimens heat treated at 850°C for 504 hours in air

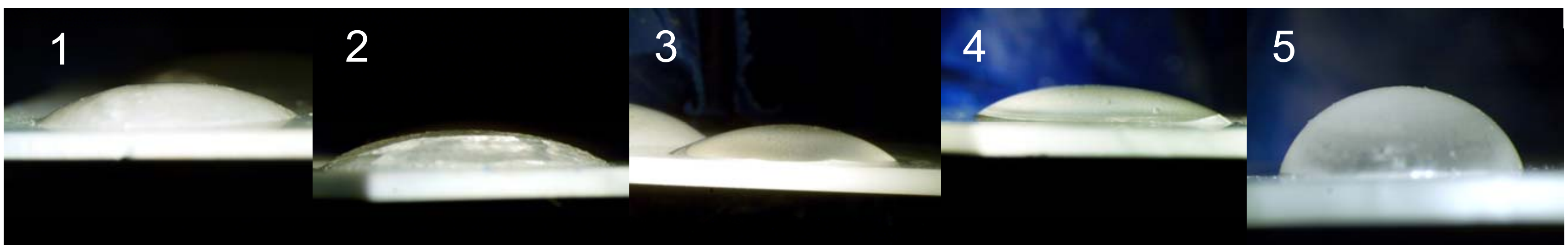
Composition (mole %)	**Crystallization**	**Flow behavior**
$19GeO_2\_76SiO_2\_5K_2O$	Mostly	Poor
$18GeO_2\_72SiO_2\_10K_2O$	Mostly	Moderate
$76GeO_2\_19SiO_2\_5K_2O$	Mostly	Moderate
$47.5GeO_2\_47.5SiO_2\_5K_2O$	**Partial**	**Good**
$90GeO_2\_5Al_2O_3\_5K_2O$	Complete	Good

Weight loss below 0.5 % in all cases

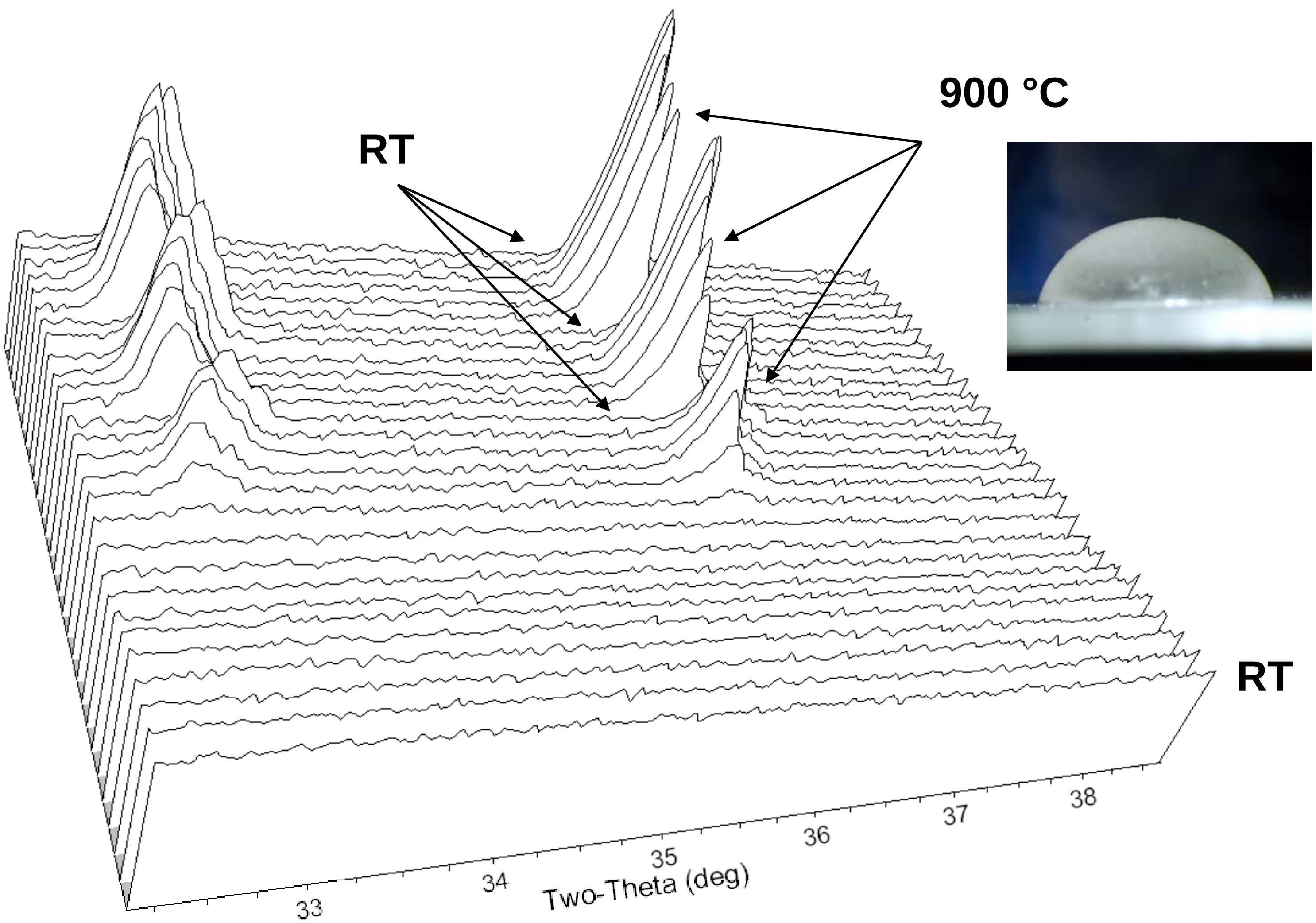
Low Tg and Excellent Flow for Modified Borogermanosilicate (BGS) Glasses

BGS glasses on Al_2O_3 after cooling to RT from 900°C

#	Composition (mole %)	Tg (°C)	Td (°C)	CTE (ppm/K) (100-400 °C)	Flow behavior (900°C)
1	$10B_2O_3$ -$10GeO_2$ $50SiO_2$ $5Na_2O$ $5K_2O$ 20ZnO	**544**	560	7.9	**excellent**
2	$10B_2O_3$ $10GeO_2$ $50SiO_2$ $5Na_2O$ $5K_2O$ 20SrO	**590**	624	10.1	**excellent**
3	$10B_2O_3$ $10GeO_2$ $50SiO_2$ $5Na_2O$ $5K_2O$ 10ZnO 10SrO	**574**	598	9.1	**excellent**
4	$10B_2O_3$ $20GeO_2$ $40SiO_2$ $5Na_2O$ $5K_2O$ 10ZnO 10SrO	**555**	590	9.04	**excellent**
5	$10B_2O_3$ $10GeO_2$ $40SiO_2$ 30SrO $10Ga_2O_3$	669	697	7.7	moderate



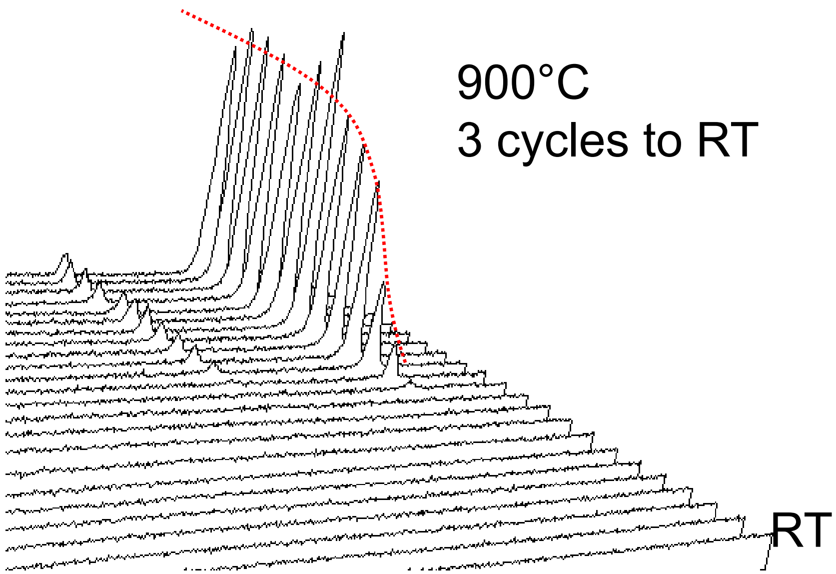
In-situ diffraction shows partial crystallization that levels off during cycling



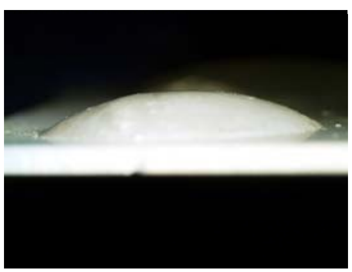
$40SiO_2$ $10B_2O_3$ $10GeO_2$ $30SrO$ $10Ga_2O_3$

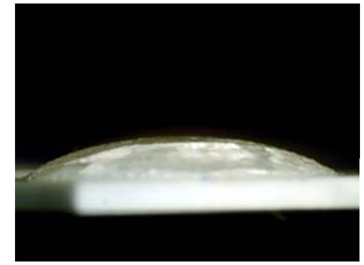
Likewise for high Zn and high Sr Ge-B-Silicates

$50SiO_2\ 10B_2O_3\ 10GeO_2\ 5Na_2O\ 5K_2O\ 20ZnO$



900°C
3 cycles to RT





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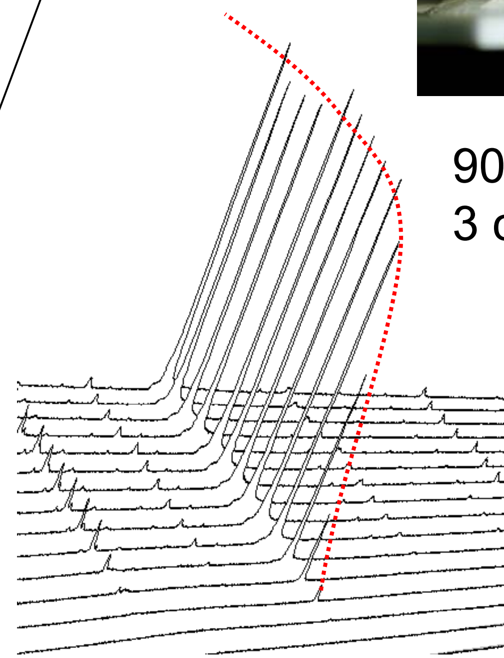
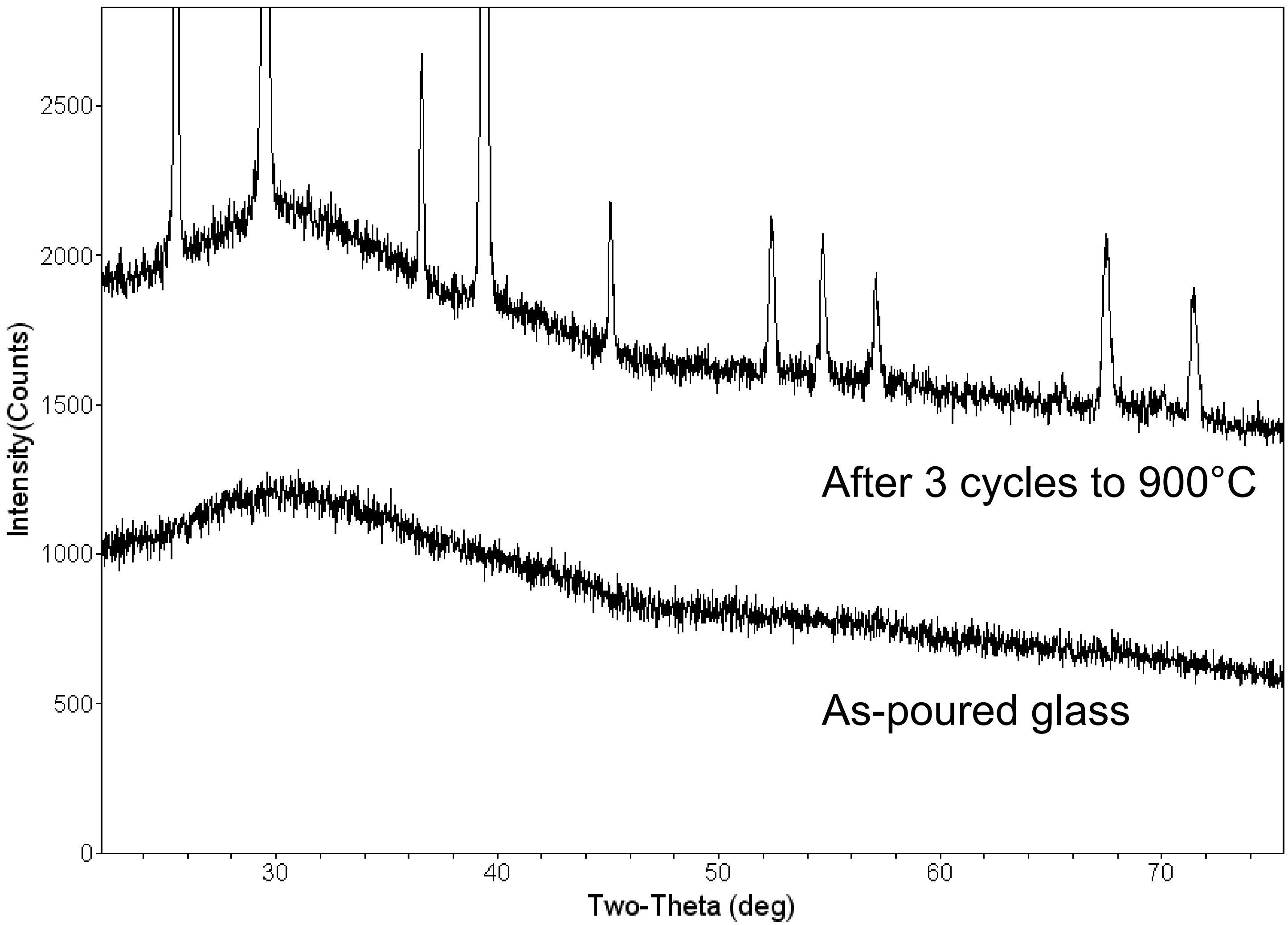


$50SiO_2\ 10B_2O_3\ 10GeO_2\ 5Na_2O\ 5K_2O\ 20SrO$

Likewise for high Zn and high Sr Ge-B-Silicates



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- Fully amorphous
  No crystallization on heating or cooling

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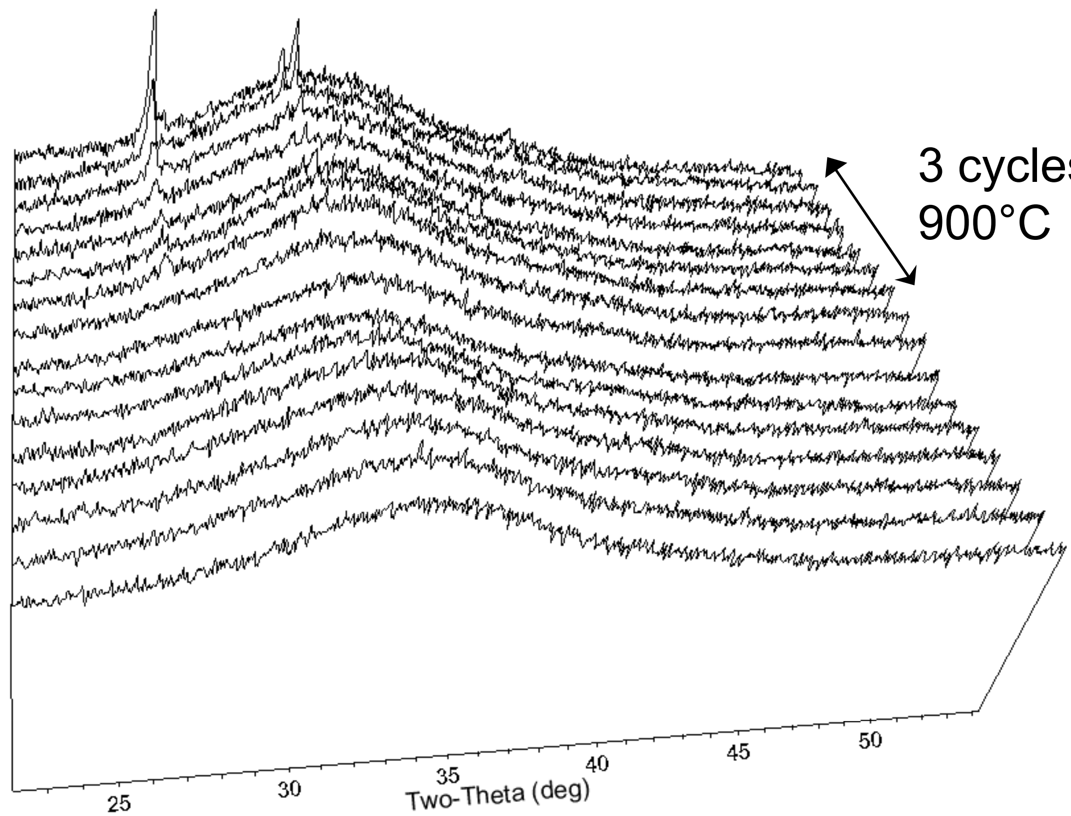
  Any crystals formed on cooling melt during heating

- Partially amorphous at operating temperature
  Remnant amorphous phase has correct viscosity and volume fraction to allow flow even with crystals present

Some of the B-Ge-Silicates and B-Ge-Ga slicates fit here

Alkaline earth gallioslicate with very limited crystallization – *possible baseline for fully amorphous sealant*



$50SiO_2$ $15Ga_2O_3$ $35SrO$

Work in Progress/Future

- Continued compositional development

  Work from downselected glasses

In parallel with additional properties measurements & characterization:

- 500 hour cycles
  - Reactivity with Al_2O_3 and YSZ
  - Weight loss
  - Percent crystallinity
  - Wetting (Al_2O_3 and YSZ)
  - Evolution of CTE, Tg, electrical conductivity, and viscosity with time

Summary: Identified Novel Glass Systems for Viscous Seals

Several new Ga silicate, Ge silicate and B-Ge silicate display promising properties:

- Viscosities of 10^3 (viscosity of honey) to 10^6 Pa·s (just softening) at 850°C
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Acknowledgements

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