Viscous Glass/Composite SOFC Sealants

Mark O. Naylor, James E. Shelby and Scott T. Misture
Kazuo Inamori School of Engineering, Alfred University, Alfred, New York

Viscous Sealant Benefits and Problems

◆ Viscous sealants allow continuous operation of SOFC stacks within the operating temperatures without the risk of brittle fracture associated with rigid sealants.

◆ Inorganic glasses and glass-ceramics are suitable for use as viscous sealants provided the compositions meet a rigorous set of requirements and remain stable for 40,000 hours at the operating temperatures.

◆ Materials knowledge for viscous sealants is currently quite limited, therefore investigation of new, untapped glass compositional space is required.

Rigorous Requirements for Viscous Sealants

- Low viscosity below 850°C while maintaining a gas tight seal above 650 C.
- Low electrical conductivity.
- Thermal stability for 40,000 hours in H_2 and O_2 atmospheres which limits the use of alkali, B_2O_3, P_2O_5, V_2O_5, and GeO_2.
- CTE match with other cell components is desirable, ~10-12 ppm/K.

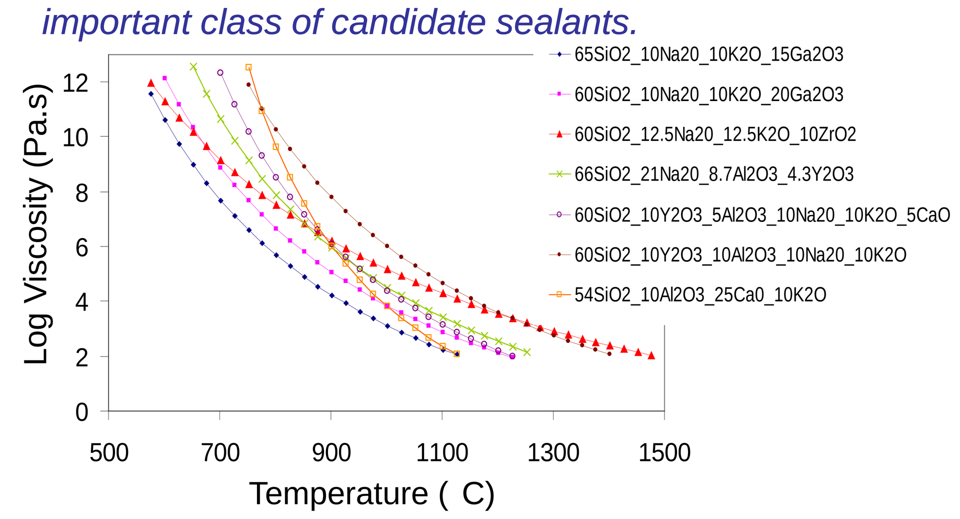
Objectives

1) Develop new glass compositions exhibiting fluidity below 850 C and Tg below ~650 C, with
   a) tunable viscosity behavior
   b) minimum alkali, alkaline earth, and B_2O_3 (?) content.
   suggests use of Ga_2O_3 and GeO_2
2) Measure thermal & chemical stability under worst case scenarios:
   a) study any crystallization or reaction products to 900 C,
   b) measure long term weight loss & stability 850 C, 500h increments.

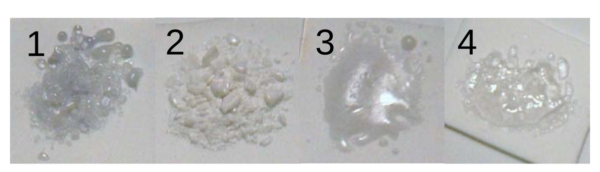
SiO_2 Glasses

An initial cross-section of all know silicates showed that glasses with potentially useful flow and CTE behavior contain 20 mol % alkali and a large fraction of Ga. Viscosity of the glasses, approximated via the Moynihan method, ranges from $10^{4.5}$ to $10^{8.5}$ Pa·s at 850 C. Observations of the glasses in powdered and bulk form show poor flow behavior, but weight loss of the glasses was less than 0.4 % after 504 hours at 850 C.

This series of silicate glasses is too viscous for use as sealants, but demonstrates that high-Ga glasses are an important class of candidate sealants.



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	1
$60SiO_2$_$10Y_2O_3$_$5Al_2O_3$_5CaO_ $10Na_2O$_$10K_2O$	**10.47**	725	755	Can be poured	2
$60SiO_2$_$10Y_2O_3$_$10Al_2O_3$_$10Na_2O$_ $10K_2O$	**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	3
$66SiO_2$_$10Y_2O_3$_$23Na_2O$	**10.49**	679	724	Easily stirred	
$65SiO_2$_$15Ga_2O_3$_$10Na_2O$_$10K_2O$	**11.79**	594	615	Flows, can not pour	4



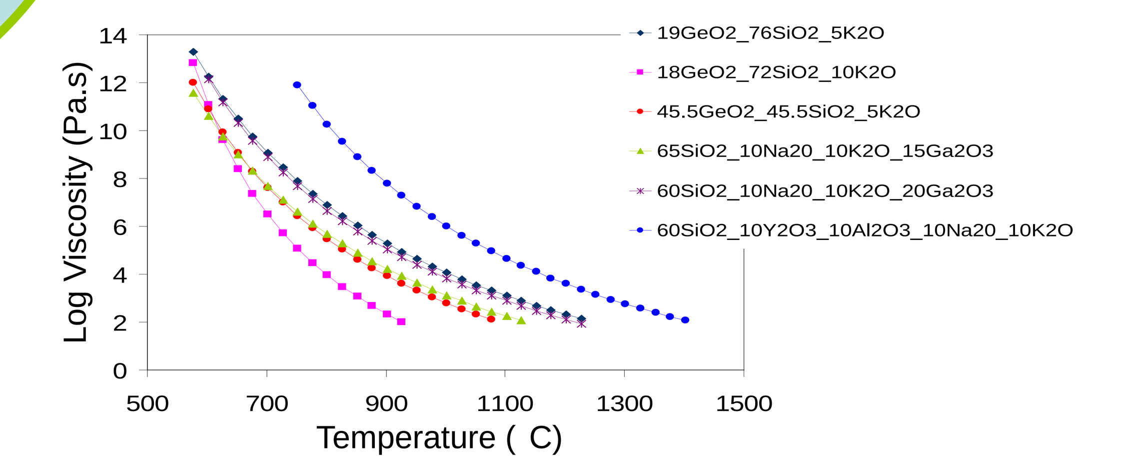
Ga_2O_3 SiO_2 Glasses

Galliosilicate glasses exhibit the lowest glass transition temperatures of the silicate glasses. Additions of SrO and ZnO successfully lowered the viscosity while decreasing the alkali content by one-half. Desirable CTE values are maintained with the alkaline earth additions. Powdered $50SiO_2$-$15Ga_2O_3$-35SrO glass strongly resists crystallization after two 30 min heat treatments at 900 C.

Composition (mole %)	Tg(C)	T_d(C)	CTE (ppm/K) (100-400 C)	Flow behavior (at 900 C)
$65SiO_2$_$15Ga_2O_3$_$10Na_2O$_$10K_2O$	594	615	11.8	None
$60SiO_2$_$20Ga_2O_3$_$10Na_2O$_$10K_2O$	640	712	11.8	None
$60SiO_2$ $15Ga_2O_3$ $5Na_2O$ $5K_2O$ 15SrO	647	698	9.2	very little
$50SiO_2$ $15Ga_2O_3$ $5Na_2O$ $5K_2O$ 25SrO	640	677	10.1	moderate
$50SiO_2$ $15Ga_2O_3$ 35SrO	760	781	8.1	none

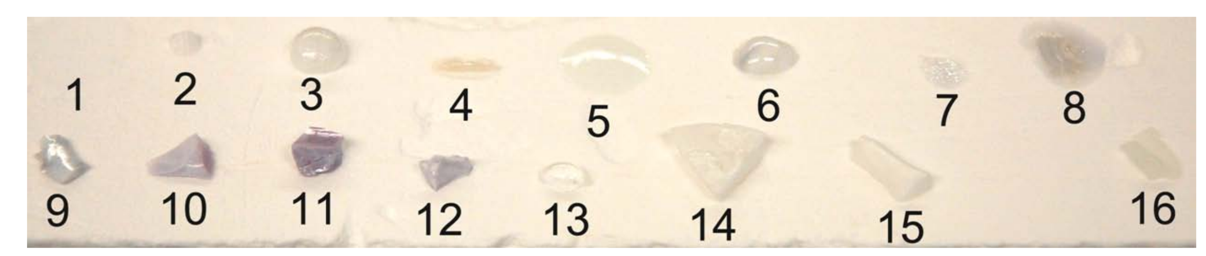
GeO_2 - SiO_2 Glasses

Germanosilicate glasses exhibit low viscosity within the SOFC operating temperature range. The viscosities of the studied compositions are much more desirable than those of the silicates, from $10^{3.8}$ to 10^6 Pa·s at 850 C. We note that high germania glasses may result in Ge metal colloids when exposed to H_2, however, additions of B_2O_3 as another glass network former may alleviate this potential problem.



#	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	Flow behavior
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

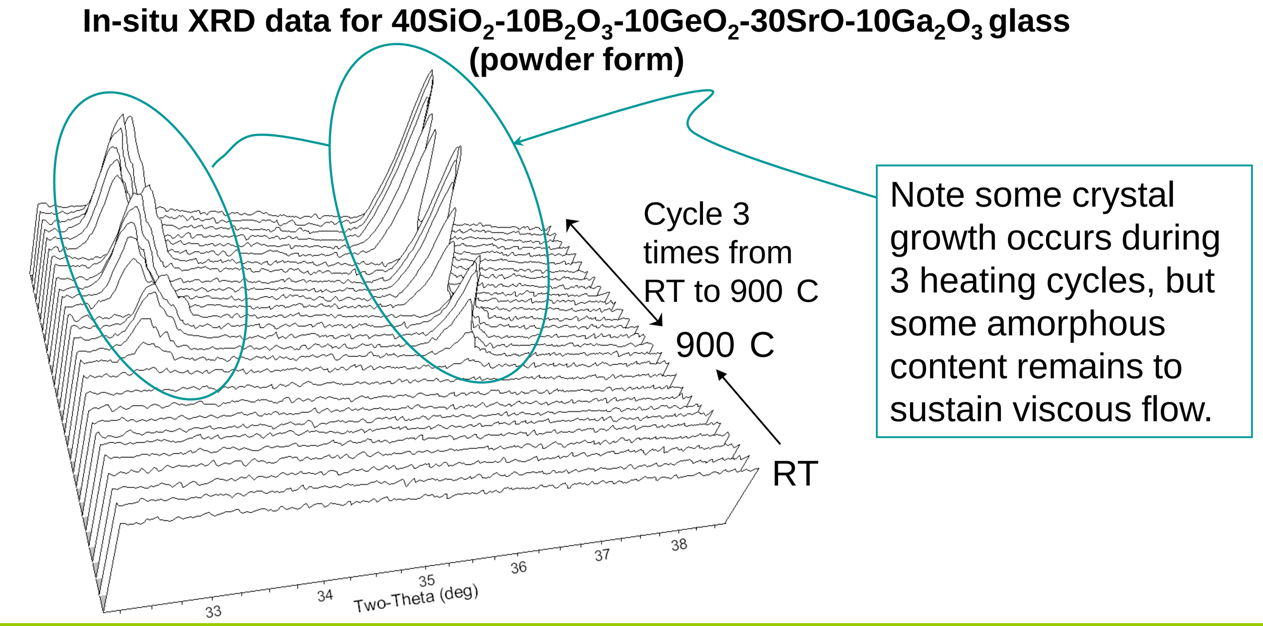


B_2O_3 GeO_2 SiO_2 Glasses

Borogermanosilicate glasses exhibit excellent flow below 900 C, showing fusing at temperatures as low as 650 C. Desirable glass transition temperatures as low as 544 C have been achieved, while CTE values are acceptable. Crystallization occurs between 800 and 900 C for some of these glasses in powdered form.

#	Composition (mole %)	Tg (C)	T_d (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 XRD data for $40SiO_2$-$10B_2O_3$-$10GeO_2$-30SrO-$10Ga_2O_3$ glass (powder form)



Conclusions

- ➢ ***Success in identifying 2 compositional regions that show applicable properties.***
- ➢ 4 borogermanosilicate (BGS) compositions exhibit flow at temperatures as low as 650 C.
- ➢ Some of these glasses retain a large fraction of remnant glass phase after several cycles from RT to 900 C, suggesting longer-term stability.
- ➢ BGS and galliosilicate compositions can exhibit Tg below 600 C with CTE values between 8 and 11 ppm/K (100 – 400 C).
- ➢ Weight losses of ~0.2 to 1 wt.% after 504 hours at 850 C noted.

Alfred University
Kazuo Inamori School of Engineering