Viscous Silicate SOFC Glass Sealants

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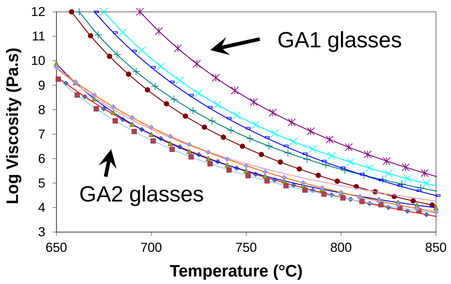
Research supported by U.S. DOE NETL: Award Number DE-NT0005177

Ga_2O_3 SiO_2 Glasses

Galliosilicate glasses exhibit low glass transition temperatures and controlled crystallization behavior. Two main compositional regions incorporate Sr and B ions with no alkali (GA1) and with 5 mole % alkali (GA2). The glasses have been compositionally designed to form seals below 900 °C.

	Alkali (mol %)	B_2O_3 (mol %)	Tg (°C)	CTE (ppm/K) (100-400 °C)	T_{seal} (°C)
GA1	0	5 - 10	660 - 710	7 - 10	≈ 850
GA2	5	5 - 10	610 - 630	8 - 10	≈ 750



Viscosity of the GA1 glasses is more fragile and remain rigid at the low end of the OT range. Viscosity behavior GA2 glasses is more optimal where these glasses flow within the entire OT range.

Viscous Sealant Benefits

- Viscous sealants allow flexibility in SOFC stack design
- Fracture is avoided at SOFC operating temperatures providing reliable electricity generation

Target Properties

- Glass transition temperatures below 600 °C
- Sealing below 900 °C
- Thermal stability for 40,000 hrs at operating temperatures between 650 and 850 °C in O_2 and H_2 environments
- Low electrical conductivity

Objectives

- Develop new glass compositions meeting DOE target properties
- Assess flow behavior of glass powders and frits
- Study interfacial reactions with SOFC stack components to monitor compatibility
- Understand crystallization behavior within SOFC OT range for long times (1500 hrs)

Compositional Modification

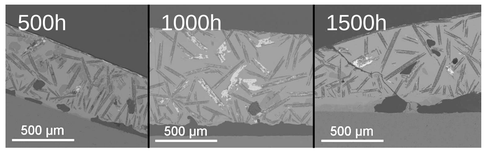
- Two main silicate systems are pursued: gallio-silicates & germano-silicates
- Modifications have been toward low or non-alkali compositions

GeO_2 SiO_2 Glasses

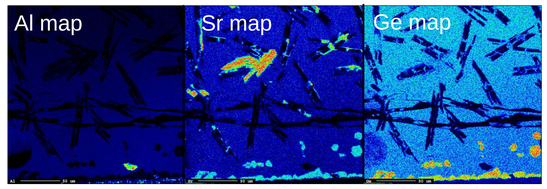
Germanosilicate glasses exhibit very low glass transition temperatures and controlled crystallization behavior. The glasses incorporate Sr and B ions with 10 mole % alkali (GE1) and with no alkali (GE2). The glasses form seals below 900 °C, where some form seals near 650 °C.

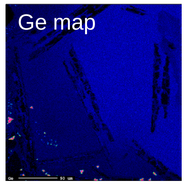
	Alkali (mol %)	B_2O_3 (mol %)	Tg (°C)	CTE (ppm/K) (100-400 °C)	T_{seal} (°C)
GE1	10	10	540 - 590	7.5 - 10	≈ 650
GE2	0	10	670	7.7	≈ 750

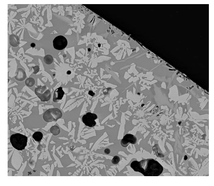
Crystallization & Reactivity



- GE1 glasses retain a very large remnant glass phase even after 1500h at 850 °C. The glasses survive 8YSZ/441SS test seals without fracture after cooling to room temperature.
- The glasses dissolve the protective alumina coatings on 441SS shown in the microprobe maps below. A $SrGeCrO_x$ phase develops at the interface.





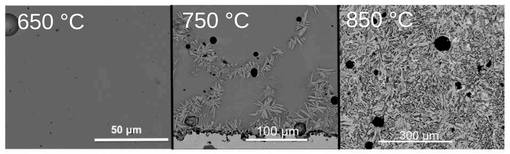


- GE1 glasses form Ge colloids in a dry H_2 atmosphere shown in the microprobe map on the left.
- GE2 glass does not form Ge colloids under the same conditions. Compositional adjustments may enable useful germanosilicate glasses for SOFC sealing.

Crystallization Within OT Range

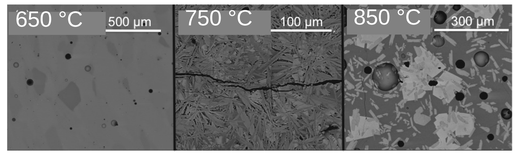
Crystallization of frit samples was tested throughout the OT range for 500 hours in air. The particle sizes are ~200 – 40 µm which allow flexibility of application techniques between stack components.

GA1 glass frit

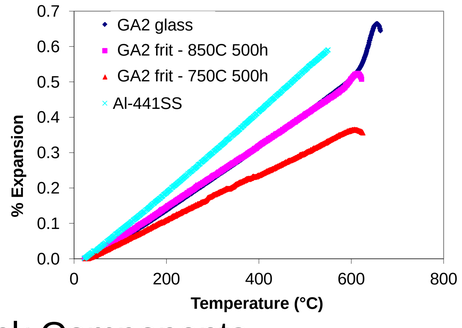


- Surface nucleation for crystal growth is noted at 750 °C, where the frit particles remain amorphous. The GA1 glasses do not crystallize at 650 °C. Crystallization is extensive at 850 °C with little remaining remnant glass.

GA2 glass frit



- Crystallization at 850 °C typically leaves ~60% remnant glass. GA2 glasses remain entirely amorphous at 650 °C. Crystallization occurs at 750 °C, yet remnant glass is present.
- Dilatometer measurements to the right show corresponding expansion values where the crystallization at 750 °C causes low CTE of the glass-ceramic.



	GA1 Glasses	GA2 Glasses	GE1 Glasses	GE2 Glasses
Possible Operating Temperatures (approximate)	750	650 / 850	650 / 750 / 850	750
Viscosity within SOFC OT range (Pa.s)	rigid - 10^5	10^{10} - 10^4	10^8 - 10^3	rigid - 10^4
Stability in reducing atmospheres	Stable	Stable	Unstable	Stable
Reactivity with SOFC stack components	Low	Acceptable	Reactive	Low

Conclusions

- Galliosilicate based glasses can allow viscous sealing of SOFC stack components. They exhibit low interaction with stack components, are stable in hydrogen environments, and have advantageous viscosities for IT fuel cells.
  - GA1 glasses appear to be excellent candidates for viscous sealants near 750 °C. Glass frits offer controlled nucleation and crystallization behavior. These glasses do not exhibit detrimental reactions with stack components at 750 °C.
  - GA2 glasses should function as viscous seals at 650 or 850 °C due to crystallization behavior of the frits. Viscosity of these glasses is ideal within the OT range, while some glass transition temperatures are below 600 °C after crystallization. Reactivity of GA2 glasses does not appear detrimental up to 1500h in air.
- Germanosilicate glasses have ideal viscosities within the OT range and excellent mechanical compatibility with stack components. Increased reactivity is observed compared to galliosilicate glasses. Stability improved with modification toward GE2 glasses.

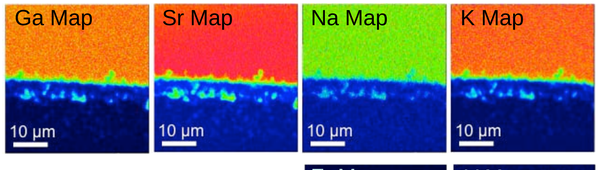
Future Work

- Extensive testing in wet H_2 environments needs to be performed to understand effects on crystallization behavior.
- Actual viscosity measurements should be made with glass and glass-ceramic samples.
- Interactions with $(MnCo)_3O_4$ coated stainless steels should be investigated.

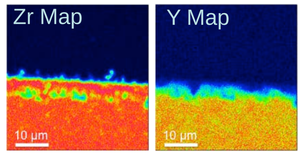
Interactions with GA2 Glasses & Stack Components

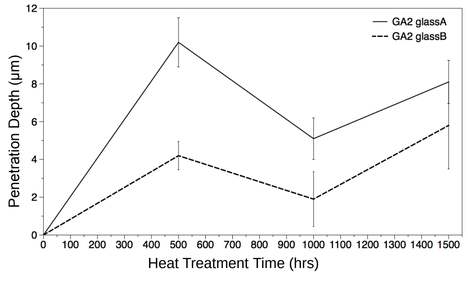
Frits of GA2 glasses were placed on 8YSZ substrates or in test seals between 8YSZ and 441SS. The samples were treated at 850 °Cfor 500h in air.

- The glass phase penetrates ~10 µm into the YSZ from the original interface. Chemistry of the diffusing glass species is not selective shown in the microprobe maps below.
- The glass does not penetrate further even after 1500h at 850 °Cas shown to the right.

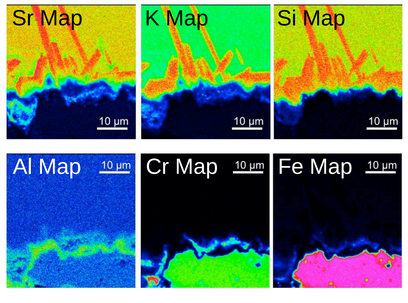


Y ions react with or diffuse into the glass more readily than Zr ions.





- Some GA2 glasses retain an amorphous interface with aluminized steel where the protective coating remains even after 500h at 850 °C shown in the Al map to the right.
- Some GA2 glasses crystallize $KSrSiO_x$ crystals along the interface shown in the upper maps. These do not cause fractures in the glass.



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