Viscous Glass/Composite SOFC Sealants

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Significant Results: Identified Two Novel Glass Systems for Viscous Seals

Some B-Ge-Si-O glasses:

- retain ~70% glass phase after 1500h at 850 °C
- partially crystallize at 850 and 650 °C
- good compatibility with Al_2O_3 and YSZ
- survive pure H_2 without Ge reduction

Some B-Ga-Si-O glass properties approach DOE targets

- glasses crystallize extensively at 850 °C
- minimal crystallization at 650 °C

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 allows flow

  - Crystals may reduce mass transport through the glass & prevent degradation over time

Initial Search for Appropriate Glass Compositions

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

High Temperature Glasses

High SiO_2 content
590 < Tg < 770°C

Gallio-silicate Glasses

10 mol% alkali
640 < Tg < 650°C

Low Temperature Glasses

Significant GeO_2 and B_2O_3 content
-excellent flow < 850°C

Germano-silicate Glasses

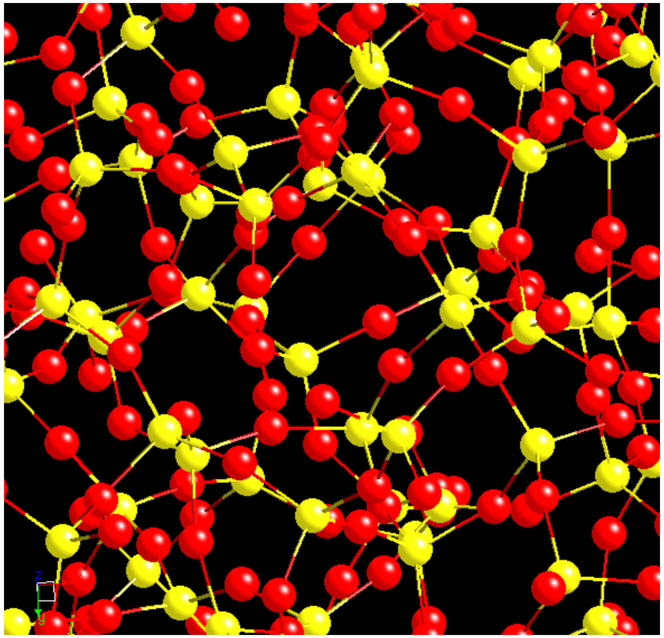
10 mol% alkali
540 < Tg < 590°C

Study both in parallel paths

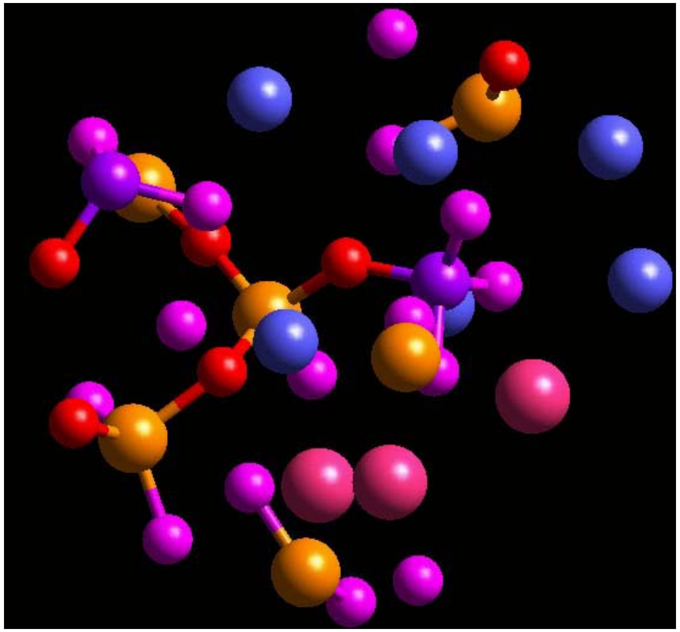
Overall Glass Composition Strategy

Maintain a high concentration of glass former

a) achieve controlled viscosity behavior
b) minimize crystallization



Vitreous network
- Controlled viscosity



Inverted structure
- Fragile viscosity
- Crystallization

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Series 1: Gallio Silicate Glasses

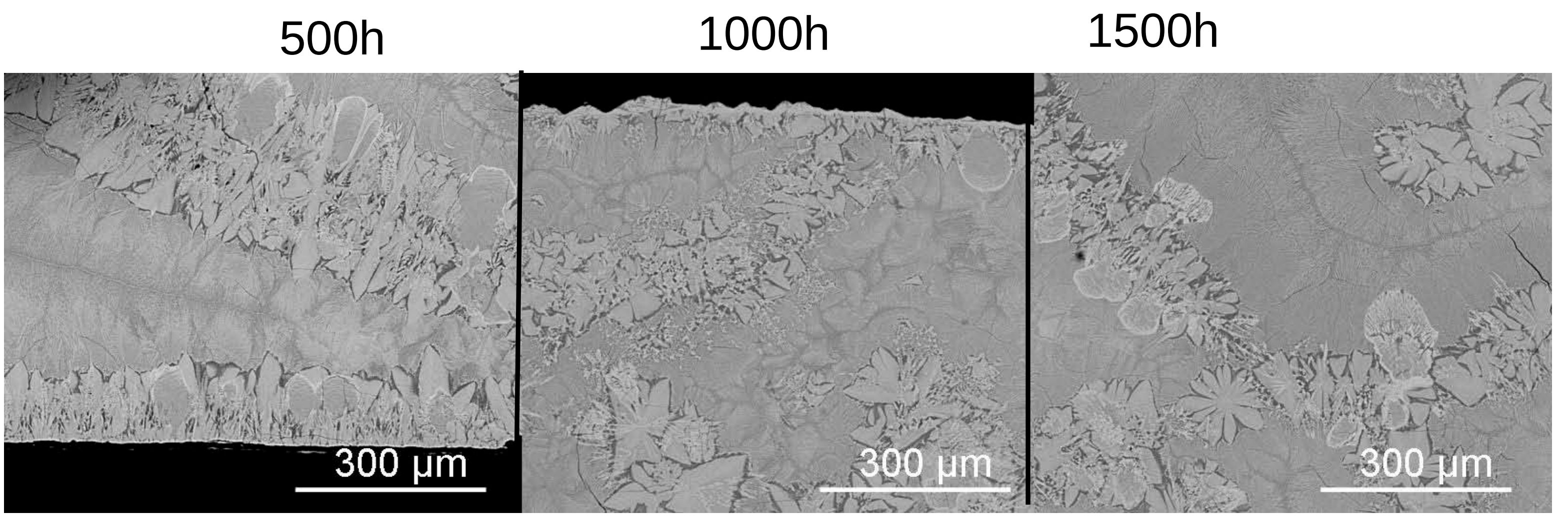
- Currently in 4th stage of compositional optimization
- Modification toward non-alkali glasses

Glass Series	Alkali (mol %)	B_2O_3 (mol %)	Tg (°C)	CTE (ppm/K) (100-400 °C)
High Temp	20	0	590 - 770	9 - 12
GaSi	10	0	640 - 650	9 - 10
GaBSi	0	5 - 10	660 - 710	7 - 10
GaBSi2	5	5 - 10	610 - 630	8 - 10
Stat Matrix	0 - 5	5 - 10		

Current iteration of optimization – full designed experiment

Many Ga-Si-B-O Crystallize Extensively at 850°C

Worst case evaluation: use glass frit and high temperature



Remnant glass nonetheless allows some flow

Crystallization inhibited at 650°C

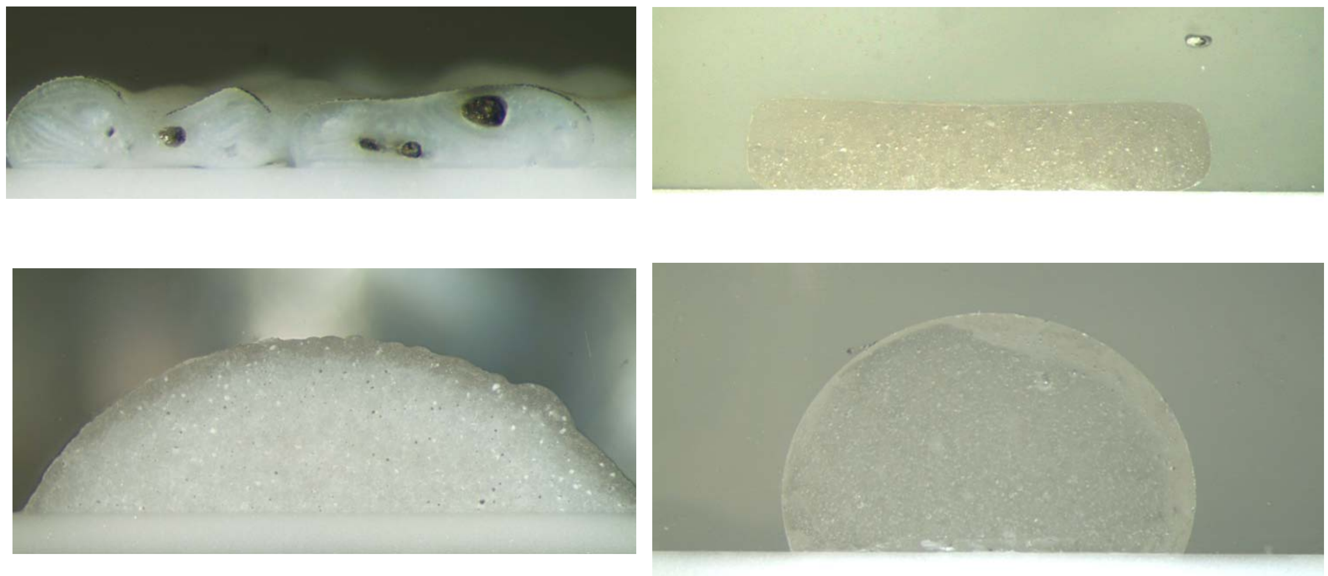
Pre-treat at 850°C for 30 min, cool to 650°C and hold for 500h

Glasses remain amorphous with heat treatment at 650°C

850°C (500h) | **650°C** (500h)

Ga-Si glass →

B-Ga-Si glass (non-alkali) →



Applicable for viscous sealing at low end OT range

Series 2: B-Ge-Si-O Glasses

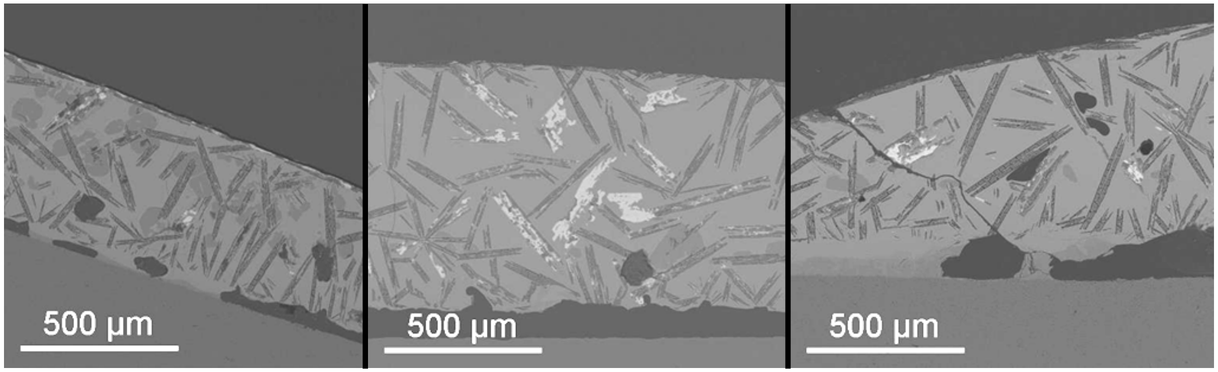
- Currently in 3rd stage of compositional adjustment
- Modification toward non-alkali glasses

Glass Series	Alkali (mol %)	B2O3 (mol %)	Tg (°C)	CTE (ppm/K) (100-400 °C)
High Temp	20	0	590 - 770	9 - 12
BGeSi	10	10	540 - 590	7.5 - 10
BGeSi2	5	10	610 - 640	8 -9
Stat Matrix	0 - 5	5 - 10		

Current iteration of optimization – full designed experiment

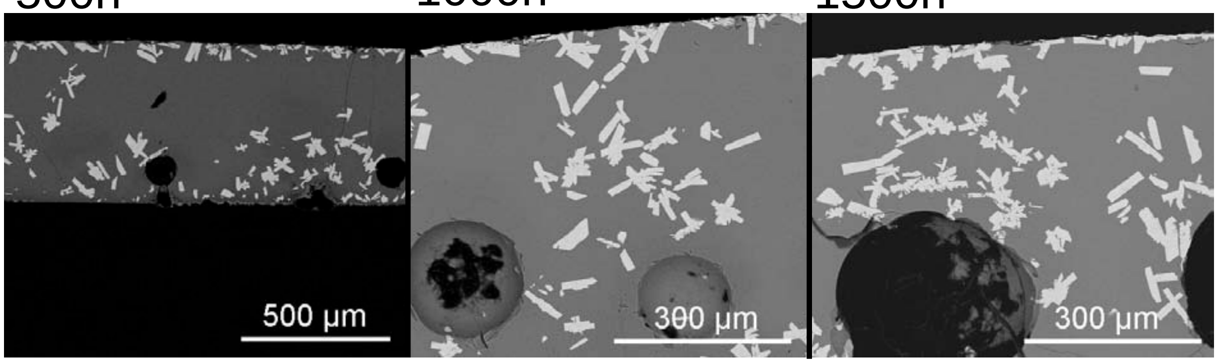
B-Ge-Si-O on Al_2O_3 retain ~70% amorphous phase after 1500h at 850°C

500h 1000h 1500h



Extensive crystallization at interface

500h 1000h 1500h

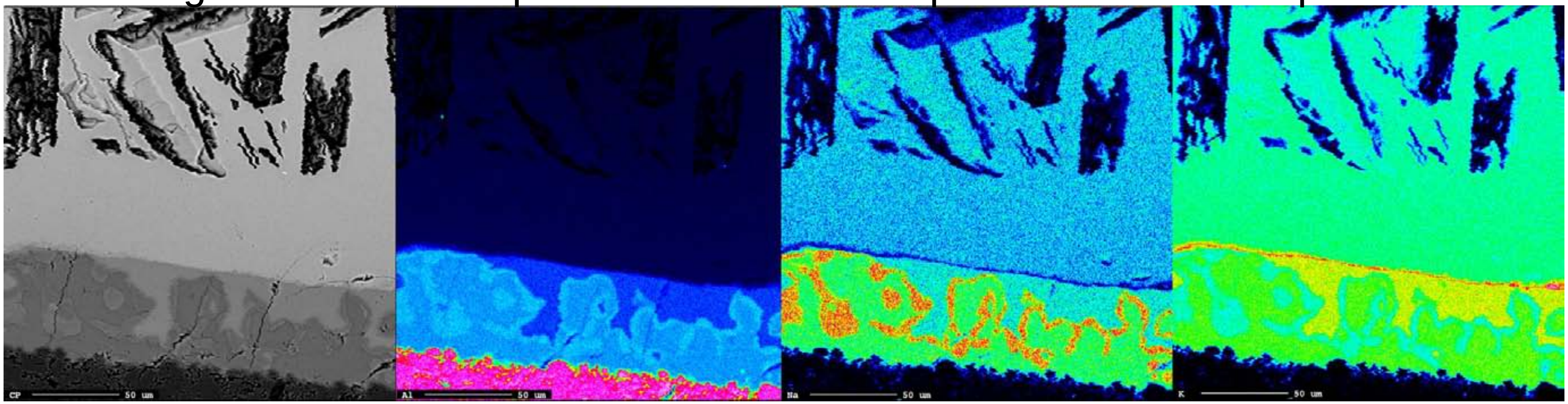


Largely amorphous interface

High Alkali Compositions Interact with Alumina

Chemical map of a B-Ge-Si glass powder on alumina after 1500h at 850°C

BSE image Al map Na map K map



• diffusion of Al into the glass
• preferential concentration of alkali at interface

Very Minor Crystallization at 650°C

Pre-treat at 850°C for 30 min, cool to 650°C and hold for 500h

Glasses partially crystalline with heat treatment at 650°C
- different morphology than at 850°C

850°C (500h) | **650°C** (500h)

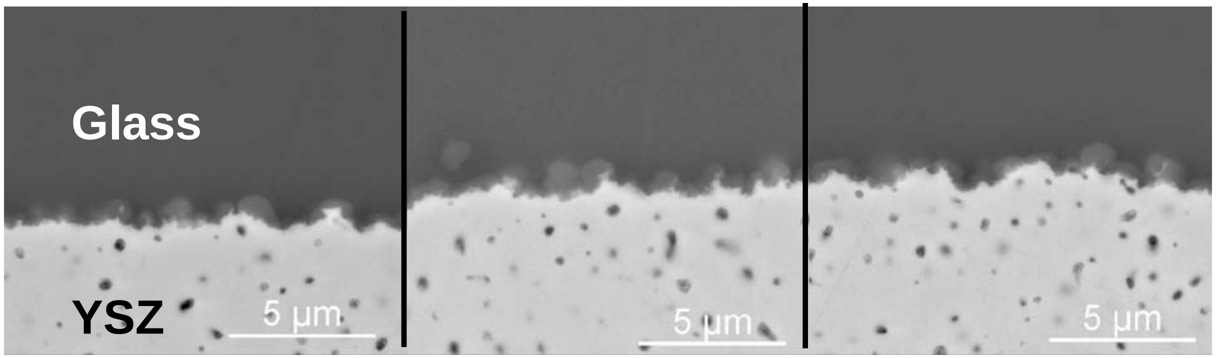
BGeSi glass →

BGeSi glass (non-alkali) →

Applicable for sealing across entire OT range, 650 to 850°C

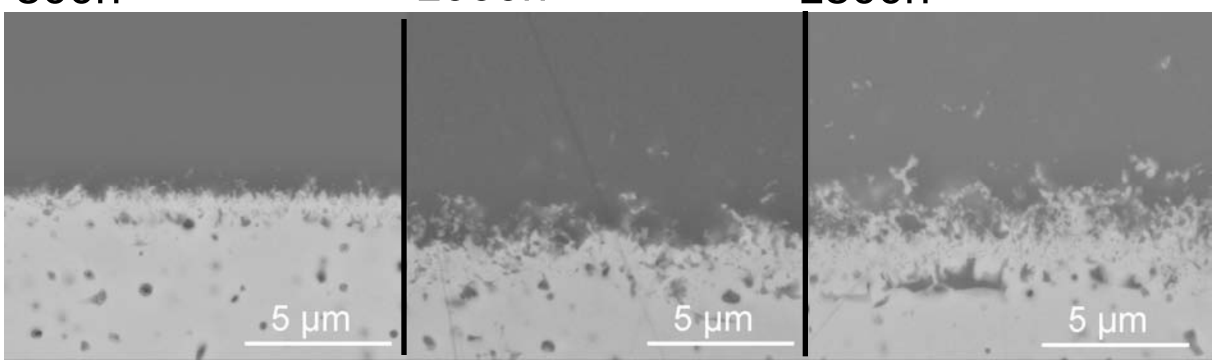
Interaction with YSZ Depends on Chemistry

500h 1000h 1500h



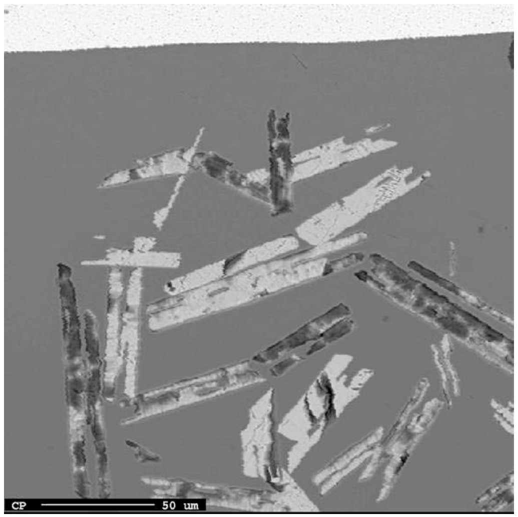
No attack of YSZ

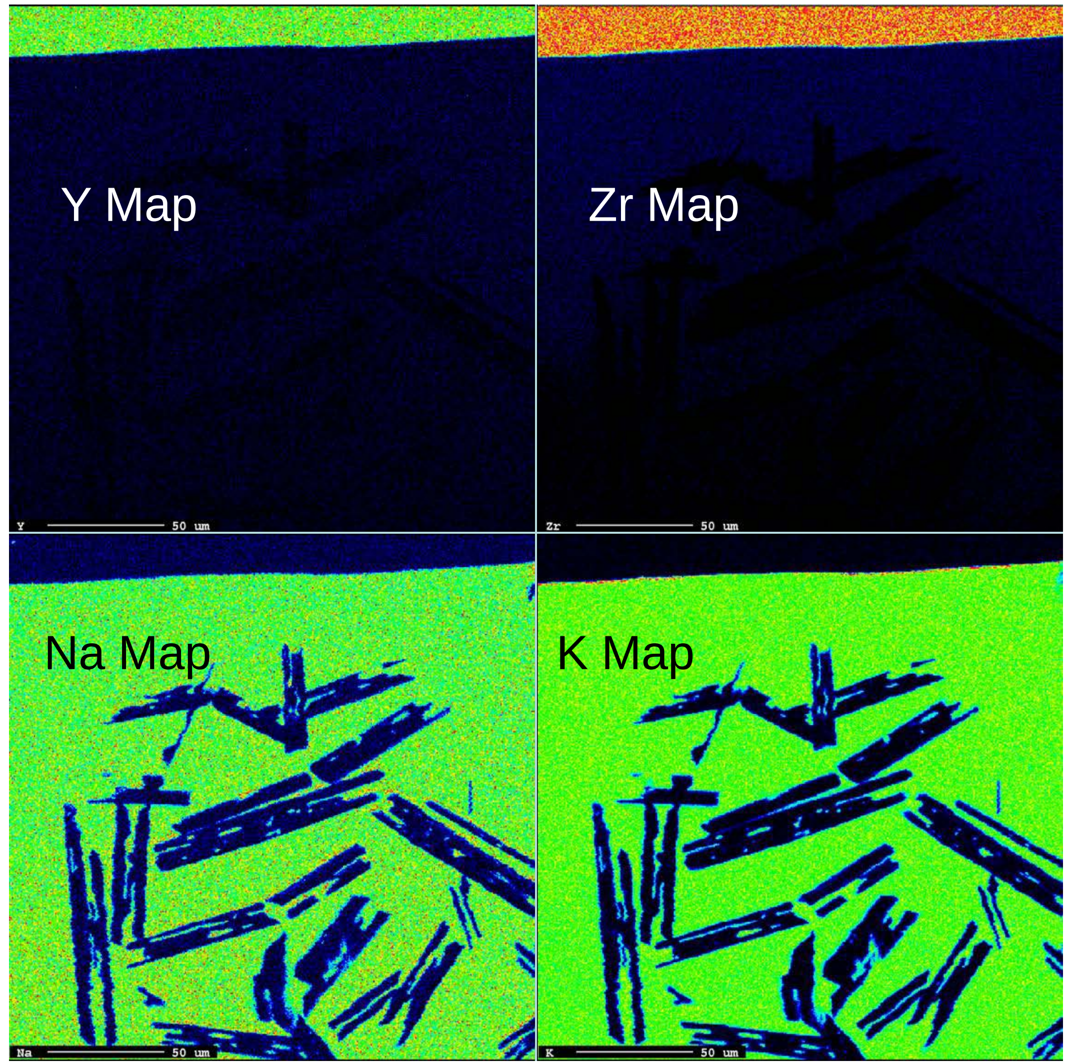
500h 1000h 1500h



Slow dissolution of YSZ

No Trace of Chemical Attack after 1000h at 850°C on YSZ

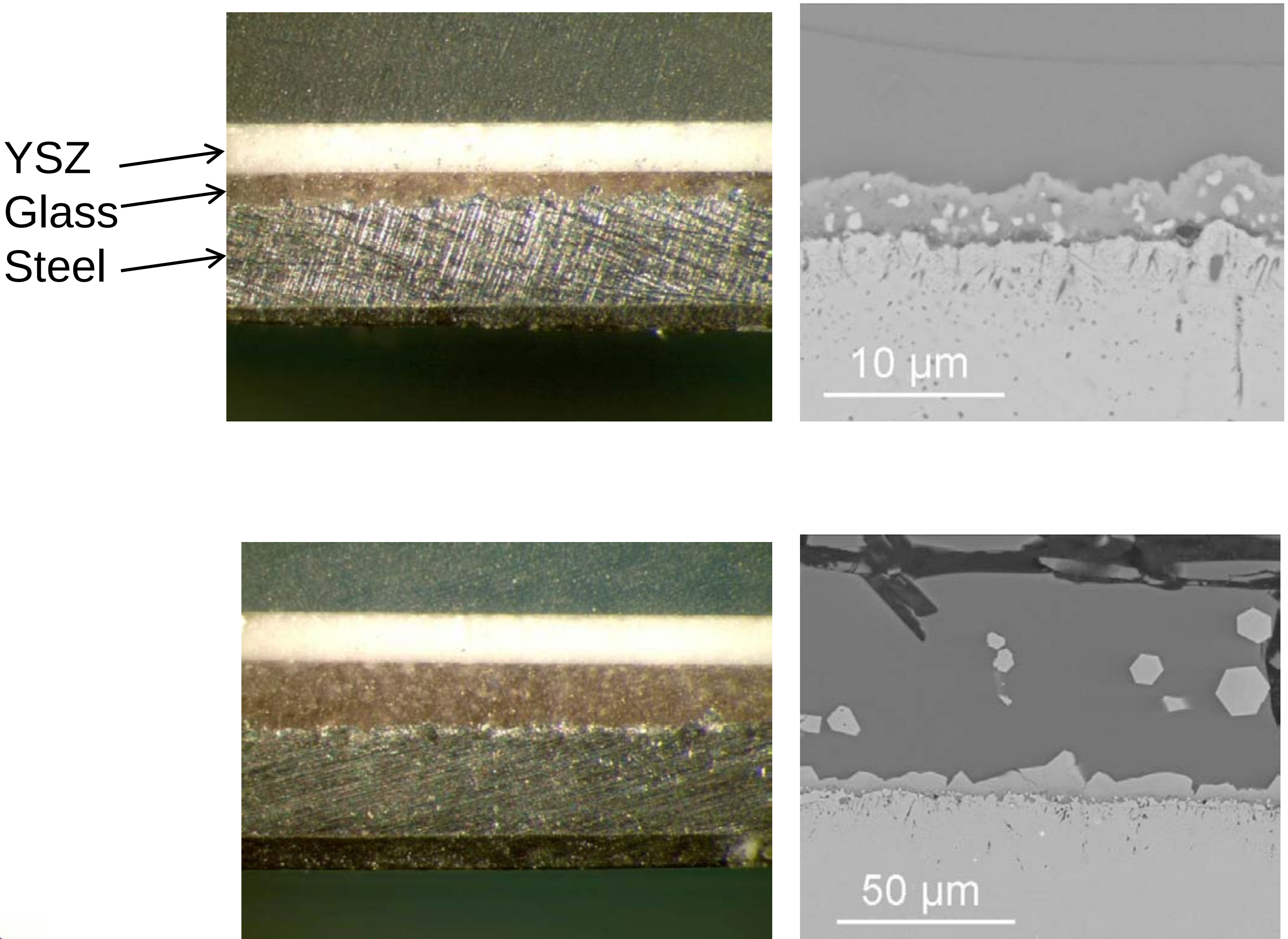




- no preferential diffusion of alkali
- no diffusion of Zr or Y into the glass

Test Seals: Aluminized SS vs. 8YSZ

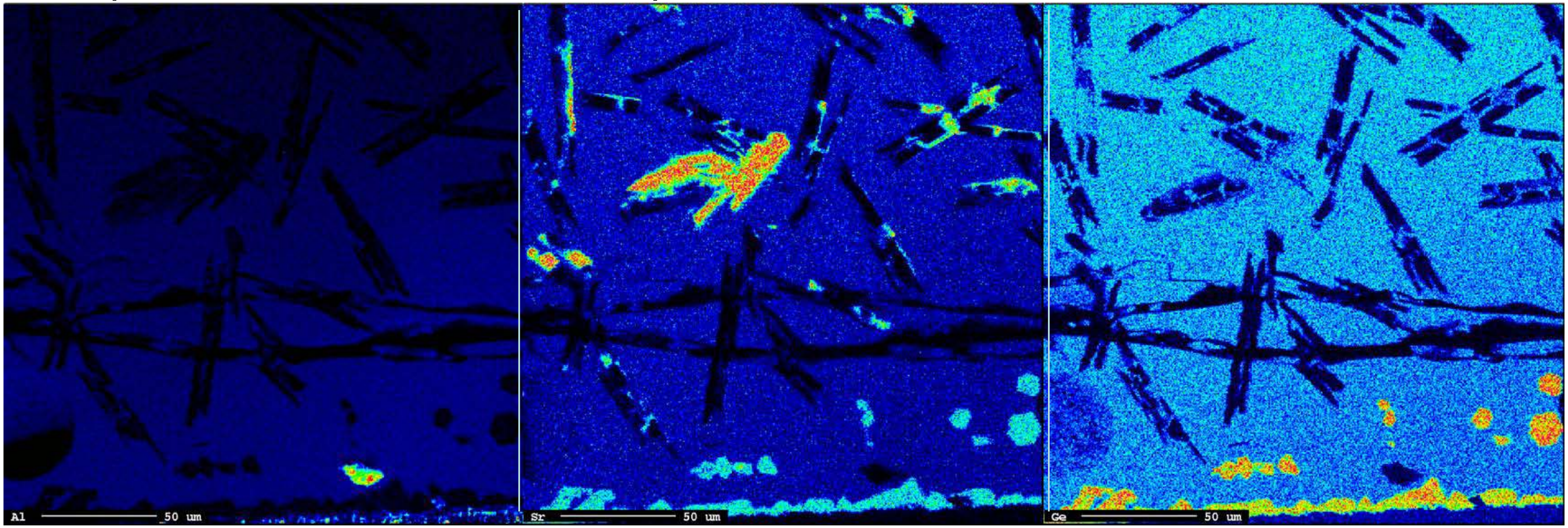
Stable on cooling from 500h at 850°C



Crystals at SS/glass interface are stable.

Some Attack of Al_2O_3 Layer Possible, Depends on Composition

Al map Sr map Ge map

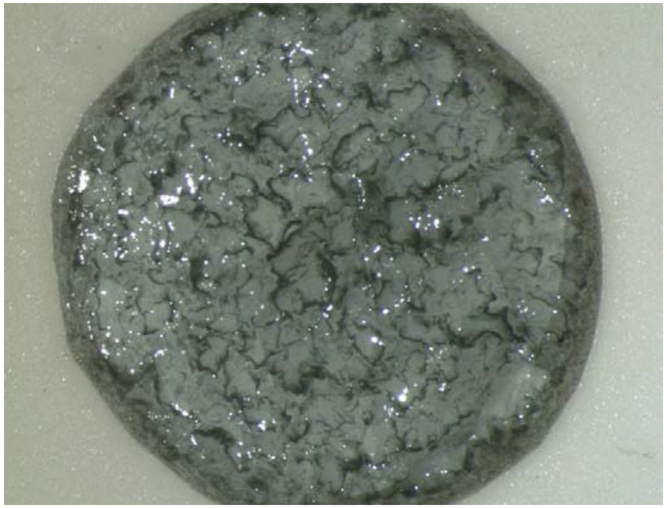


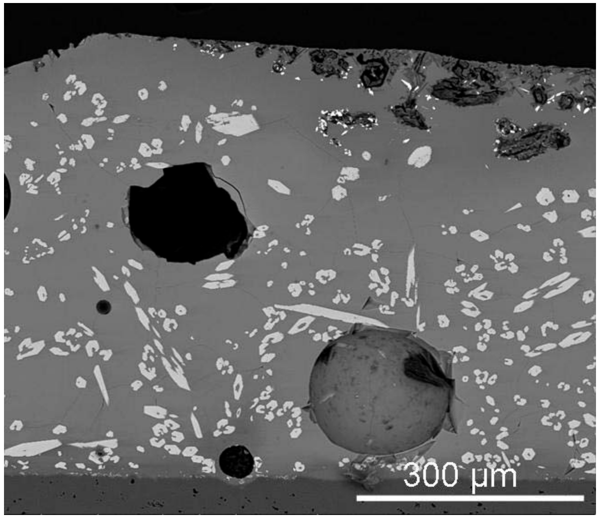
Note Ge enrichment at interface – good or bad?

Initial H_2 Testing – Zn is Unstable

Zn containing B-Ge-Si glasses heat treated at 830°C in 1 atm H_2 for 3 days

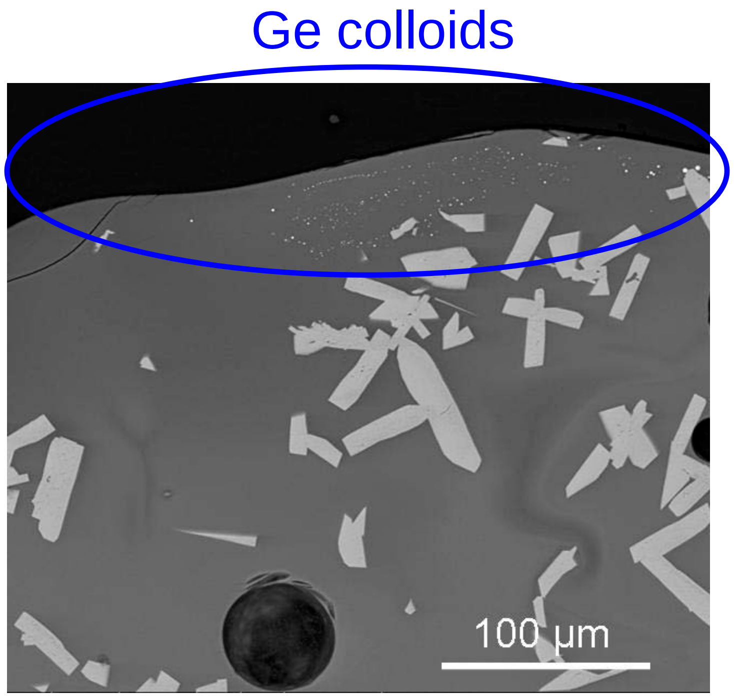
- Highly volatile Zn
- Ge colloid formation



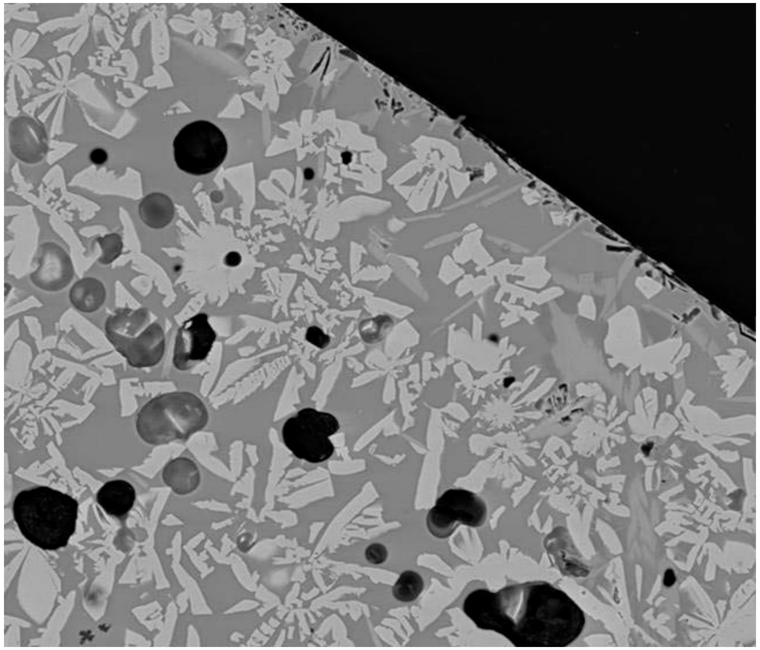


High Alkali Results in Ge Colloid Formation in Surfaces

- Ge colloid formation on surface
- Colloid layer ~100 μm deep



Low Alkali B-Ge-Si Glasses Stable Under Pure H_2



B-Ge at Low Alkali Levels

Alkali (mol %)	B_2O_3 (mol %)	Tg (°C)	CTE (ppm/K) (100-400 °C)
5	10	610 - 640	8 -9

Glasses thus far:

- retain high amorphous content to enable viscous seals
- inhibit Ge colloid formation

New Glass Compositions: Statistical Design

Matrix incorporates gallio and germano-silicate glasses

- **9 component glass compositions**

Should offer optimized properties in these systems

- some non-alkali glasses
- some glasses with no GeO_2

Alkali (mol %)	B_2O_3 (mol %)
0 – 5	5 - 10

Summary of Top Candidate Glasses

Some B-Ge-Si-O glasses are promising for 650 – 850°C range

- retain ~70% glass phase after 1500h at 850°C
- partially crystallize at 850 and 650°C
- good compatibility with Al_2O_3 and YSZ
- survive pure H_2 without Ge reduction

Some B-Ga-Si-O glass properties approach DOE targets – in particular for lower temperature range

- glasses crystallize extensively at 850°C
- minimal crystallization at 650°C

Future Work

For existing 2 series of glasses:

• Additional stability studies at 650°C

• Extensive testing in humidified H_2

For new glasses:

• Study the new 9-component glasses defined by statistical design

Identify the critical compositional component ranges for viscous flow and resistance to H_2 degradation

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