Viscous Glass Sealants for Solid Oxide Fuel Cells

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Overview of Results

1. Non-alkali boro-gallio-silicates seal between 750 and 850 °C
   1. Possible OT around 750 °C
   2. Crystallization is extensive at 850 °C
   3. Retain a large fraction of remnant glass at 750 °C for viscous flow

2. Low alkali boro-gallio-silicates seal between 650 and 850 °C
   1. Possible OT from 650 °C to 850 °C
   2. Crystallization is extensive at 750 °C, but remnant glass remains
   3. Low reactivity with SOFC stack components

3. Boro-germano-silicates seal between 650 and 850 °C
   1. Best thermomechanical match with SOFC stack components
   2. Ideal viscosity behavior
   3. Potential for Ge reduction by H_2

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

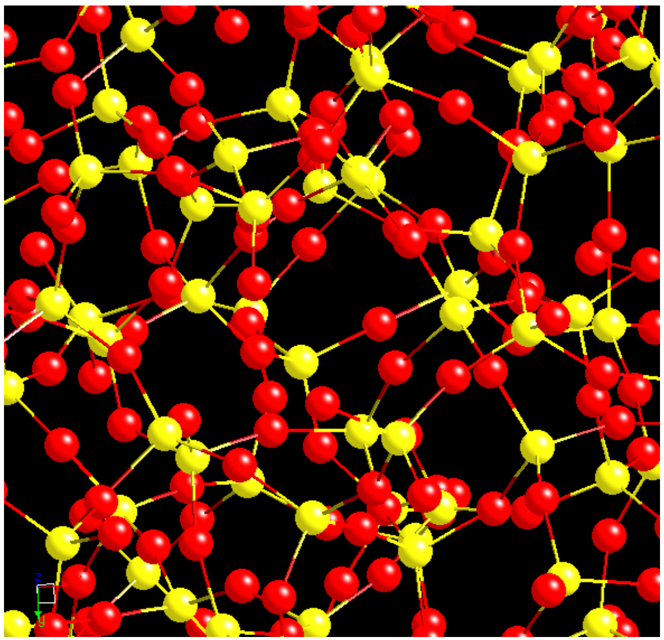
- Partially amorphous at operating temperature
  Remnant amorphous phase allows flow

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

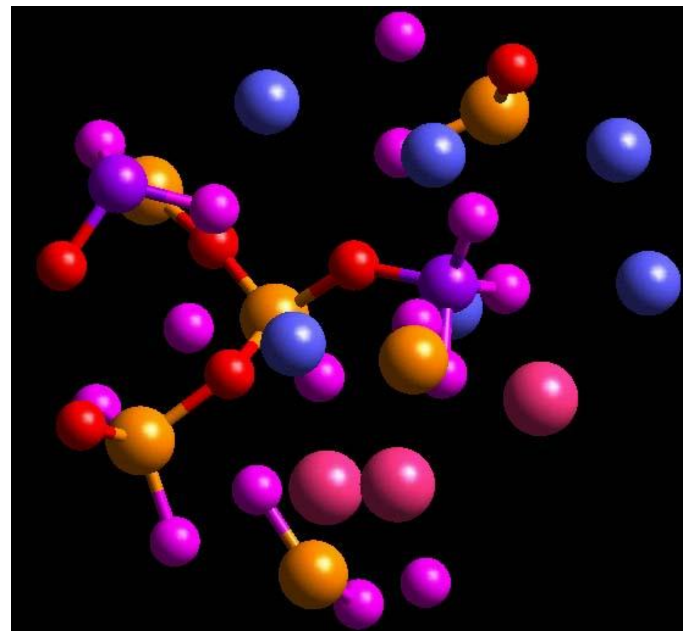
Overall Glass Composition Strategy

Maintain a high concentration of glass former

a) achieve controlled viscosity behavior
b) minimize crystallization



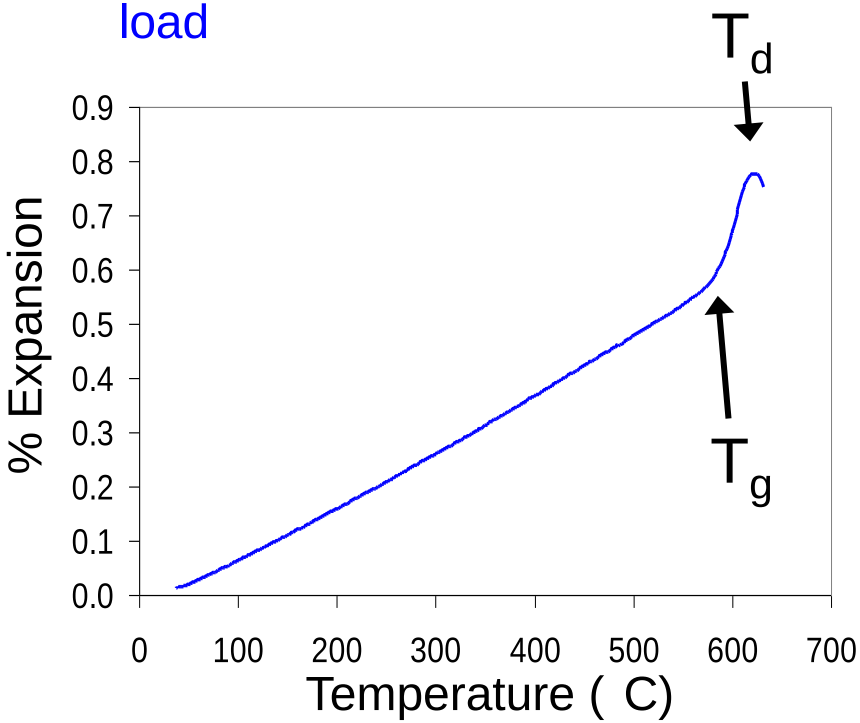
Vitreous network
- Controlled viscosity

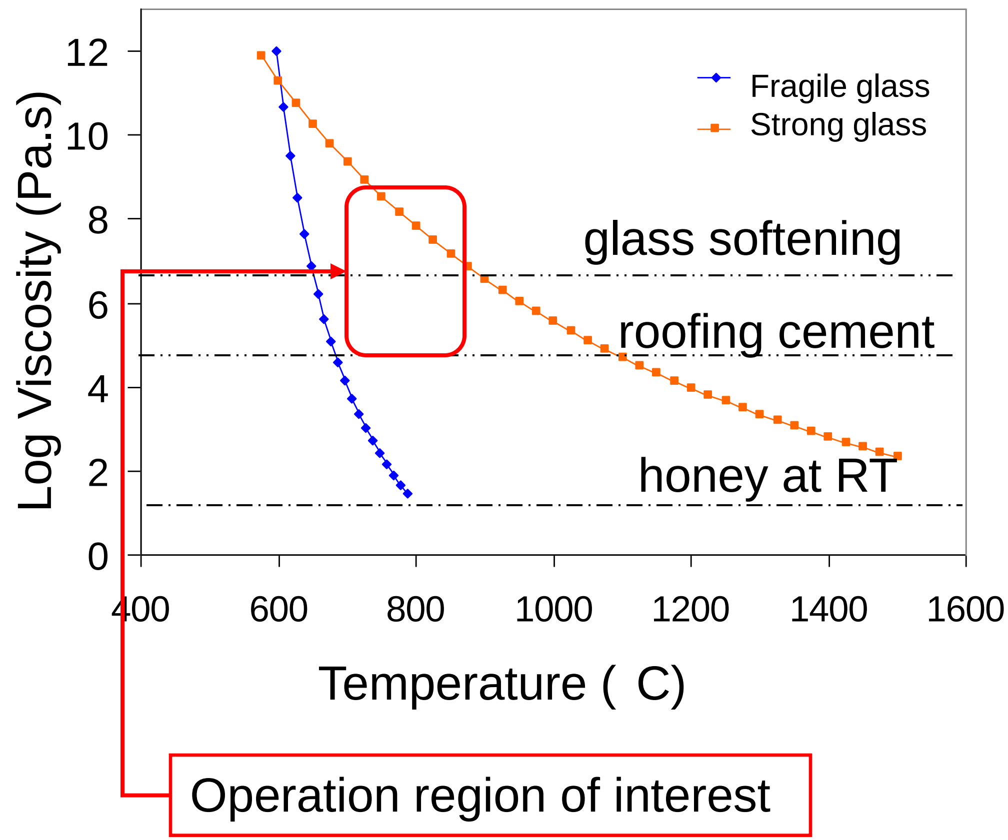


Inverted structure
- Fragile viscosity
- Crystallization

Overview of “viscous” – softening and viscosity

Dilatometry data – expansion and flow of glass under small load





Overall Logic: 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 to reduce alkali

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

First 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

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

Glass Composition Development

Alkali 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

↓

Substitute alkaline earth for alkali

↓

Ga_2O_3 additions

Tg: 540 – 590 C

Alkali Ga_2O_3 SiO_2

Strong viscosity behavior

↓

Substitute alkaline earth for alkali

Sealing <900 C

↓

Substitute B_2O_3 for remaining alkali

↓

Small additions of alkali

Tg: 610 – 690 C

GallioSilicate Compositional Modifications

- 3rd and 4th stage of compositional adjustment
- Modification toward non-alkali glasses

Glass Series	Alkali (mol %)	B_2O_3 (mol %)	Tg (C)	CTE (ppm/K) (100-400 C)	Tseal (C)
High Temp	20	<10	590 - 770	9 - 12	> 950
GaSi	10	<10	640 - 650	9 - 10	≈ 900
GaBSi	0	<10	660 - 710	7 - 10	≈ 850
GaBSi2	5	<10	610 - 630	8 - 10	≈ 750

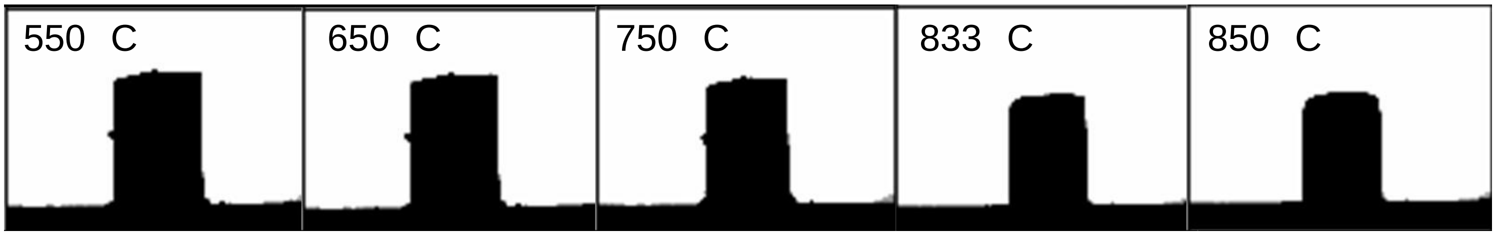
Encouraging results:

- T_{seal} decreases with decreasing alkali content
- Tg approaches 600 C with only 5 mol% alkali

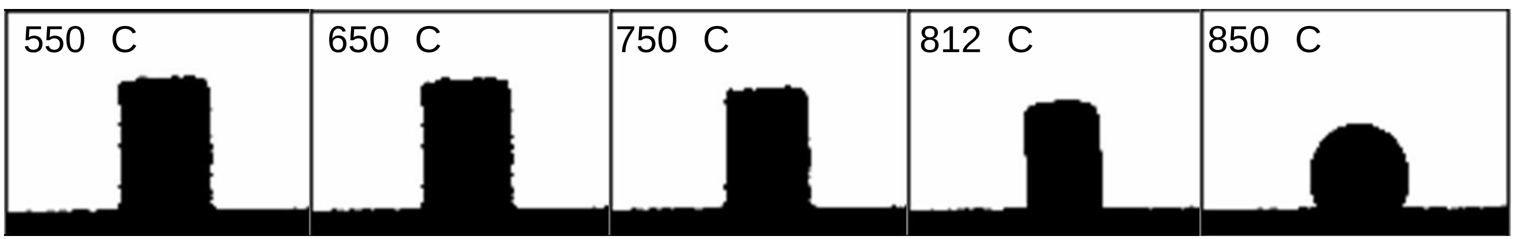
Additions of Boron to Improve Flow Behavior

Hot Stage Microscopy:

Press <50 µm glass powder into 3 mm pellet



GaSi glass: no significant flow before 850 C



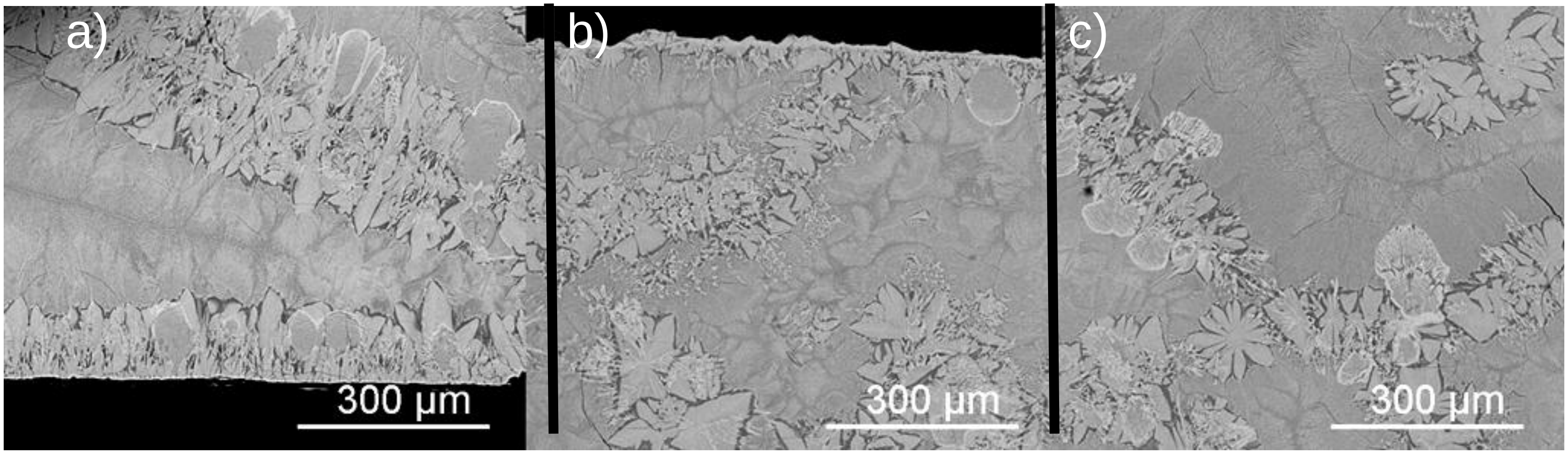
GaBSi glass: significant flow before 850 C

Achieved improved flow with non-alkali GaBSi glasses

Alkali Gallio-Silicate Glasses

Frit samples on alumina
Extensive crystallization after 504 hrs at 850 C
High thermal stability of microstructure, yet little remnant glass phase

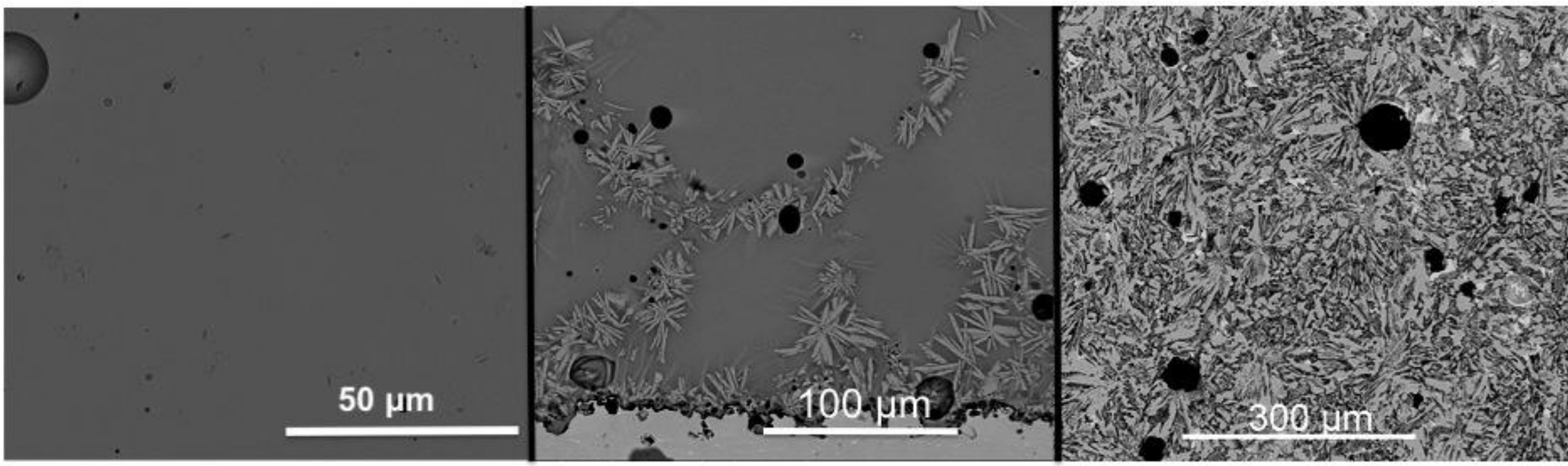
500 hrs → 1000 hrs → 1500 hrs



Alkaline Earth Boro-Gallio-Silicate Glasses

Frit samples
Varied crystallization after 500 hrs at each temperature

650 C | 750 C | 850 C

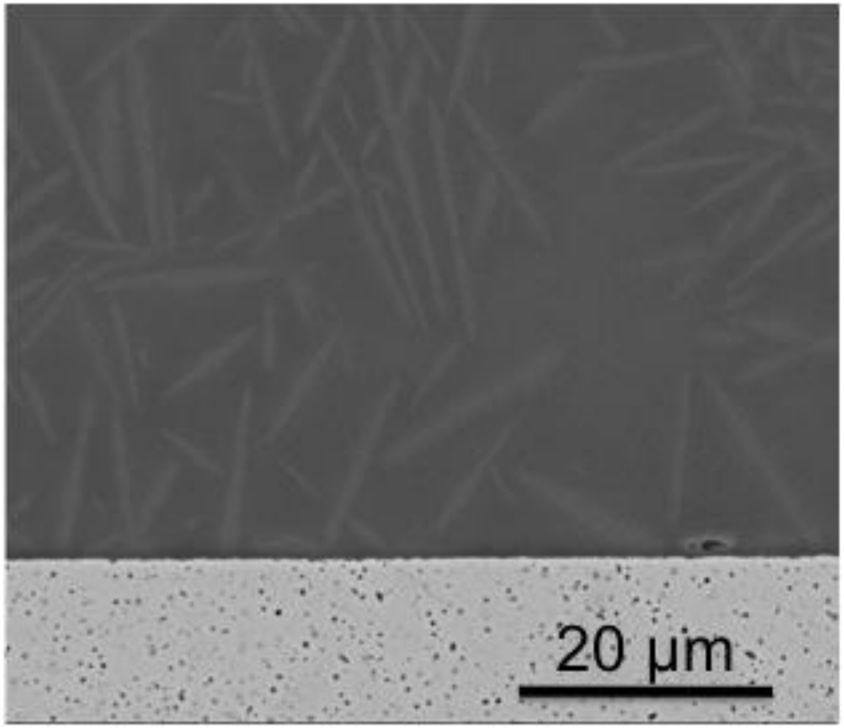


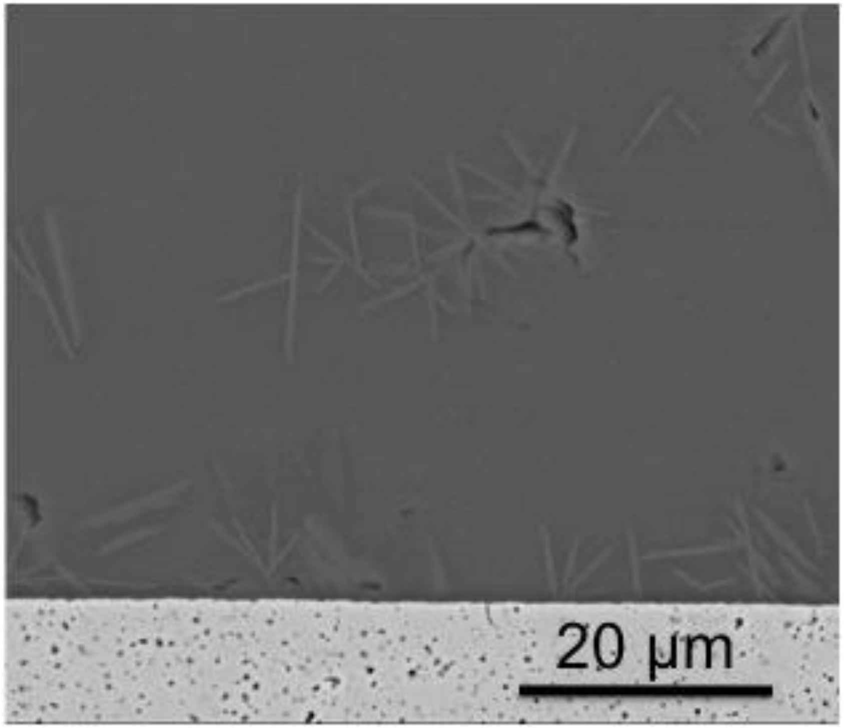
Fully amorphous | Largely crystalline

Alkaline Earth Boro-Gallio-Silicate Glasses

Low reactivity with electrolytes after 500h at 750 C

- crystallization at interface

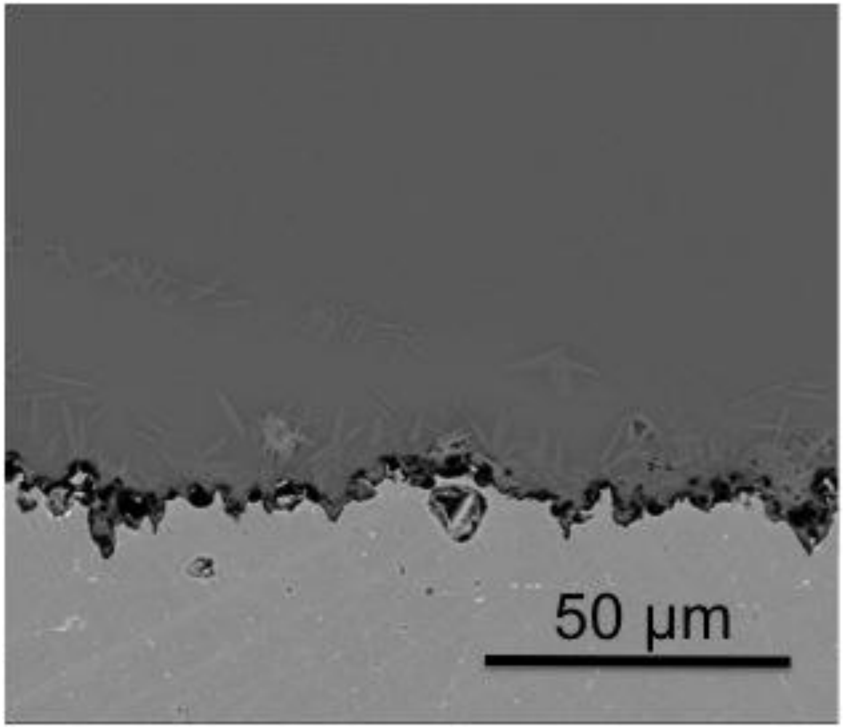


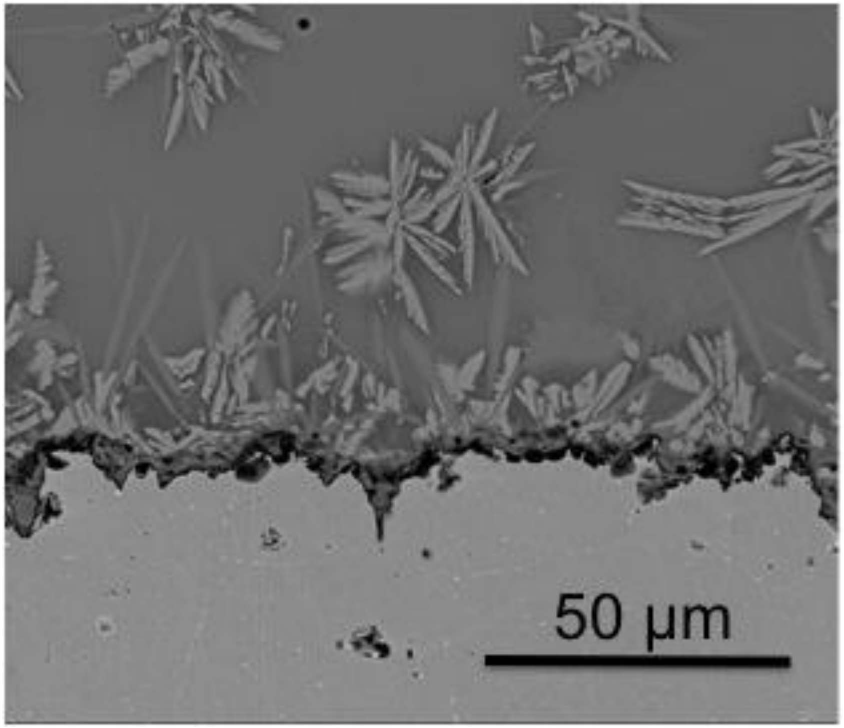


Alkaline Earth Boro Gallio-Silicate Glasses

Compatibility with protective Al_2O_3 coatings: 500h at 750 C

- crystallization at interface

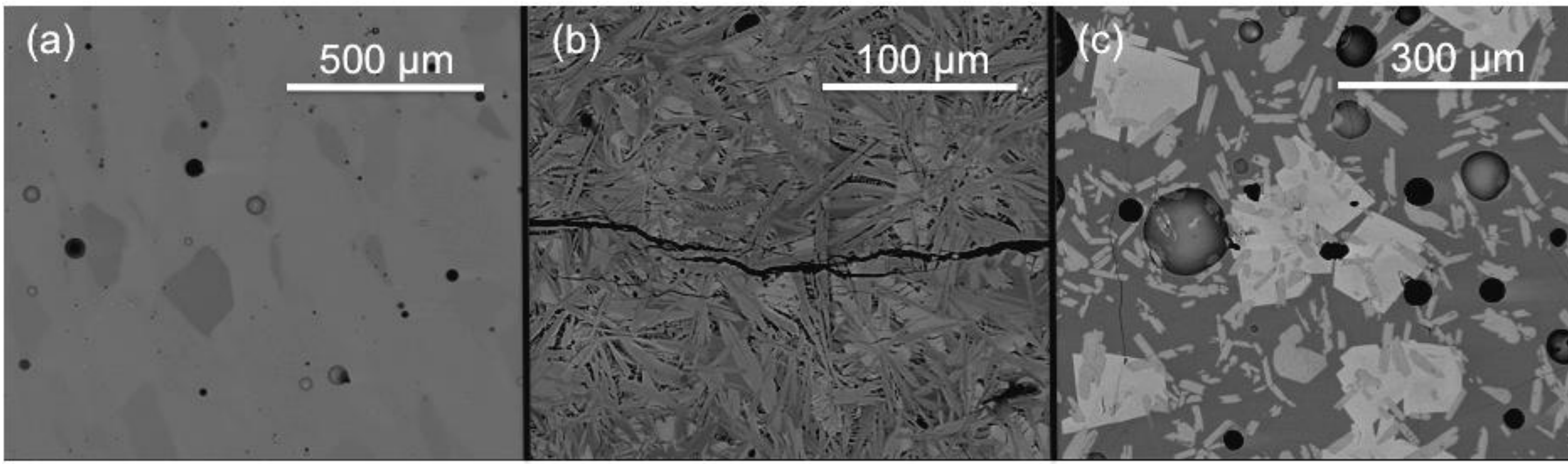




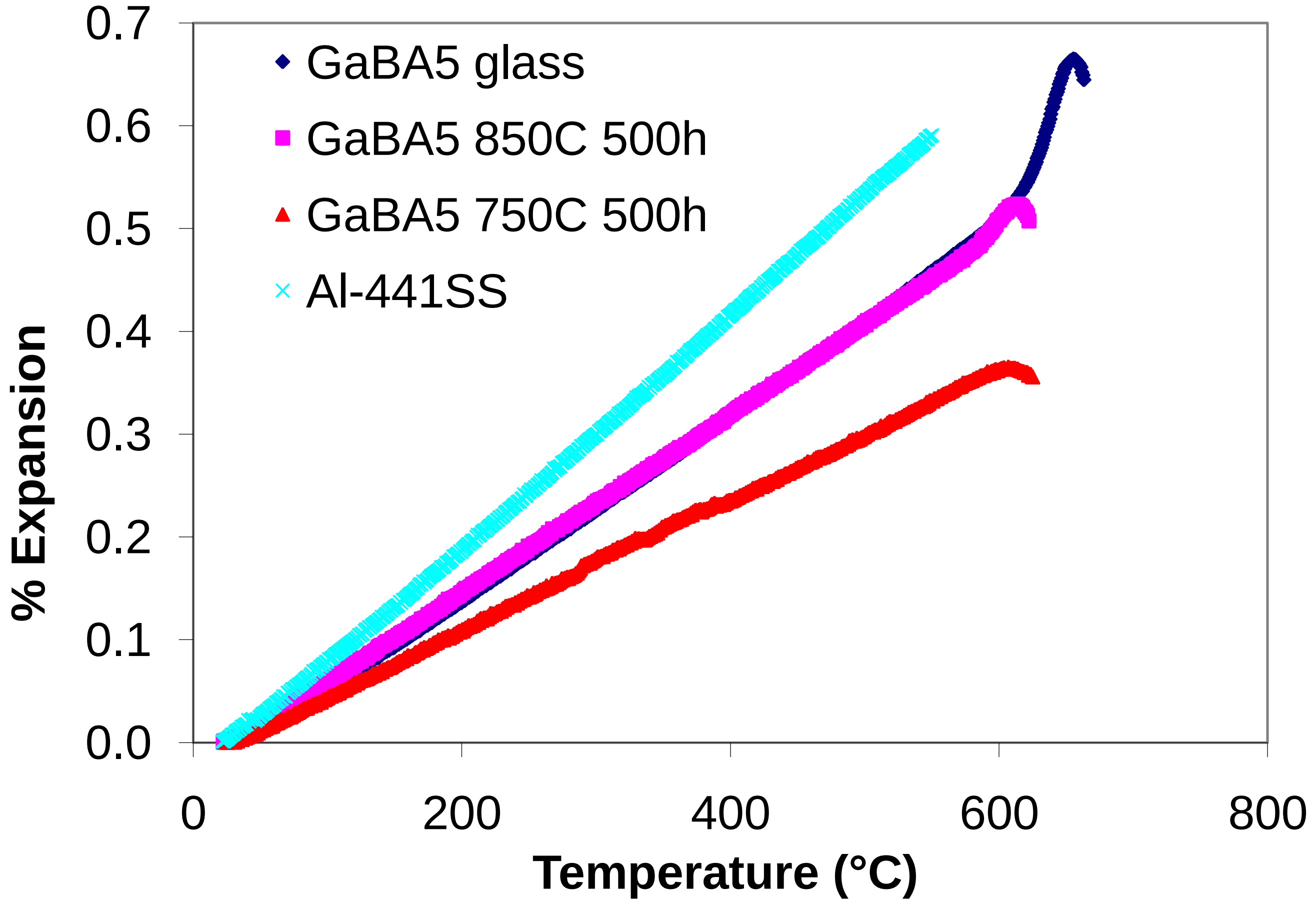
Low Alkali Boro Gallio-Silicate Glasses

Frit samples
Varied crystallization after 500 hrs at each temperature

650 C 750 C 850 C



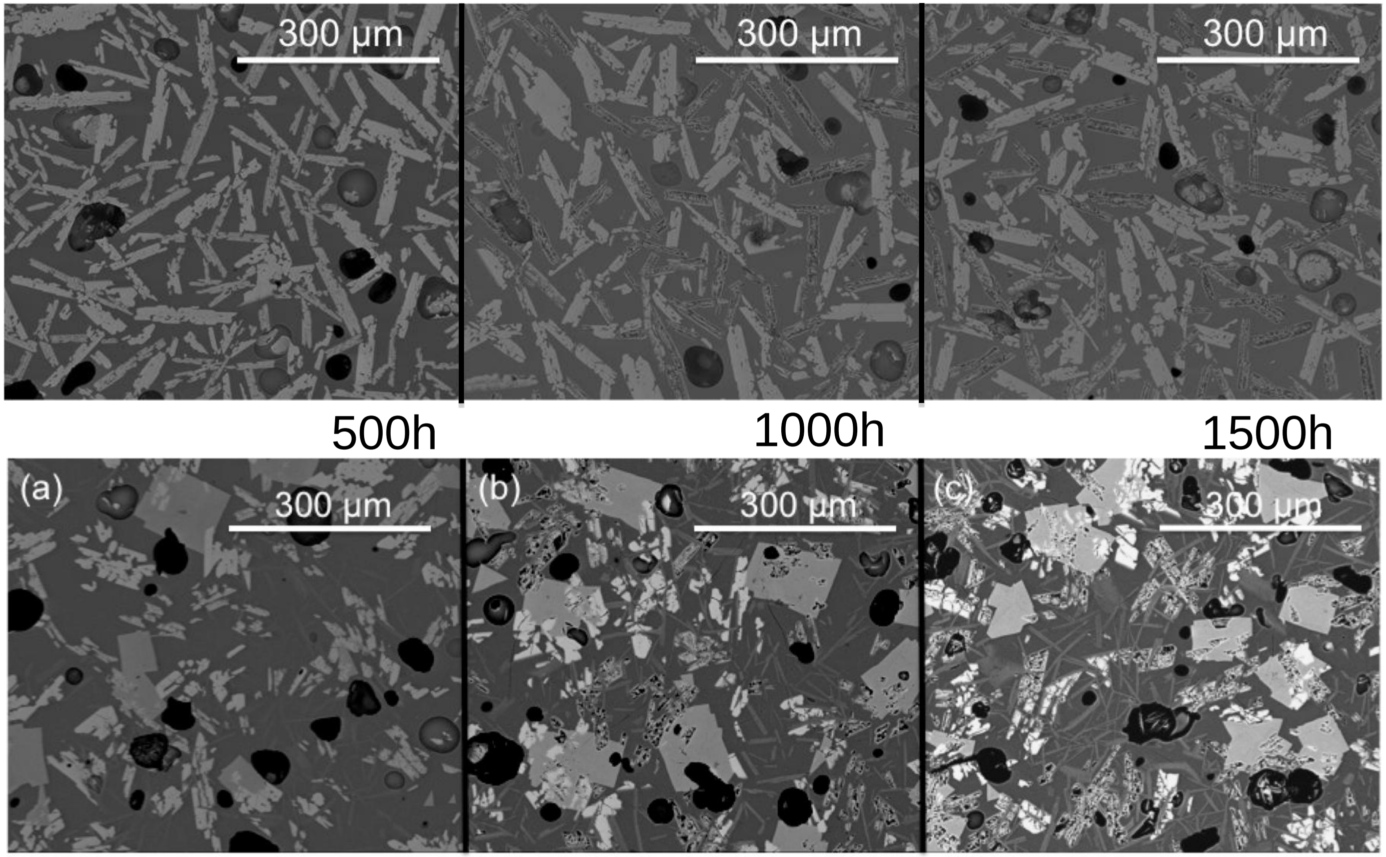
Crystallization Affects Thermal Expansion Behavior



Varied Crystallization Behavior

≈ 60% amorphous

Retain high amorphous content after 1500h at 850 C and 3 thermal cycles to RT

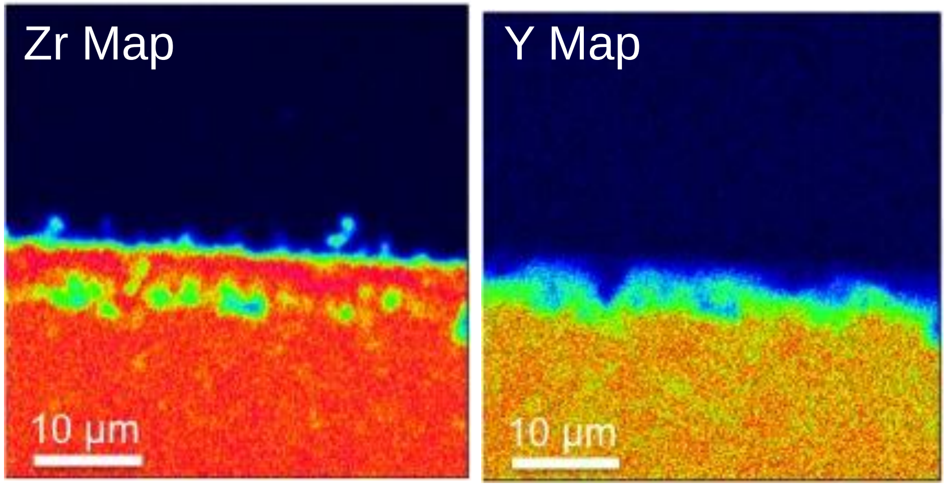


Remnant glass crystallizes on reheating to 850 C

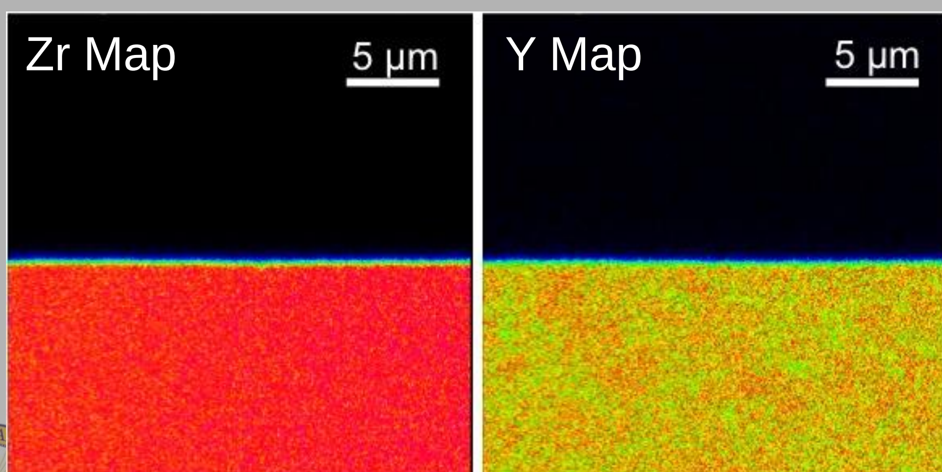
Need to study temperature cycling further

Reactivity is Temperature Dependent

850 C 500h



850 C 30 min, 650 C 500h



Low alkali boro-gallio-silicates

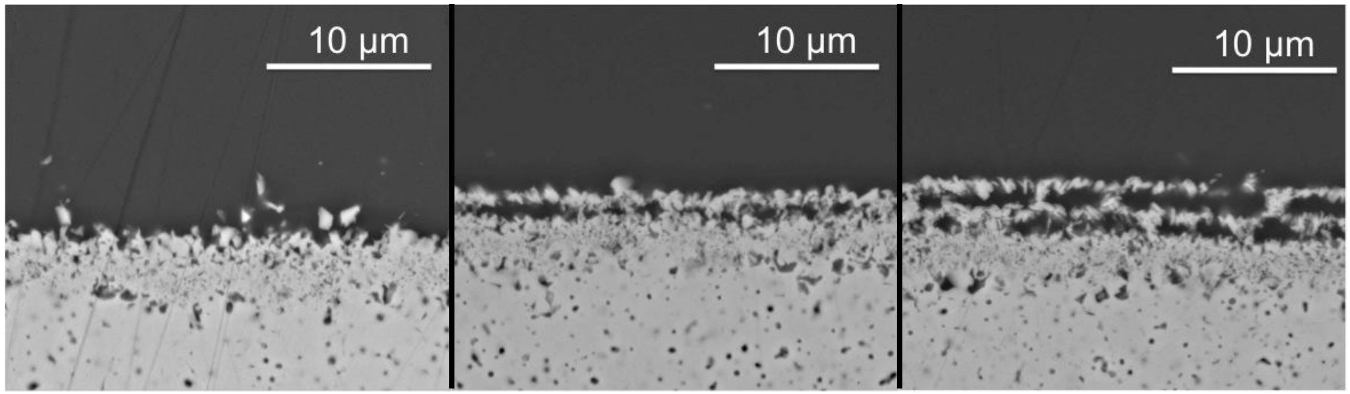
Lower interaction at 650 C:

- Sharp interface
- No penetration via grain boundaries

Interactions with 8YSZ Substrates

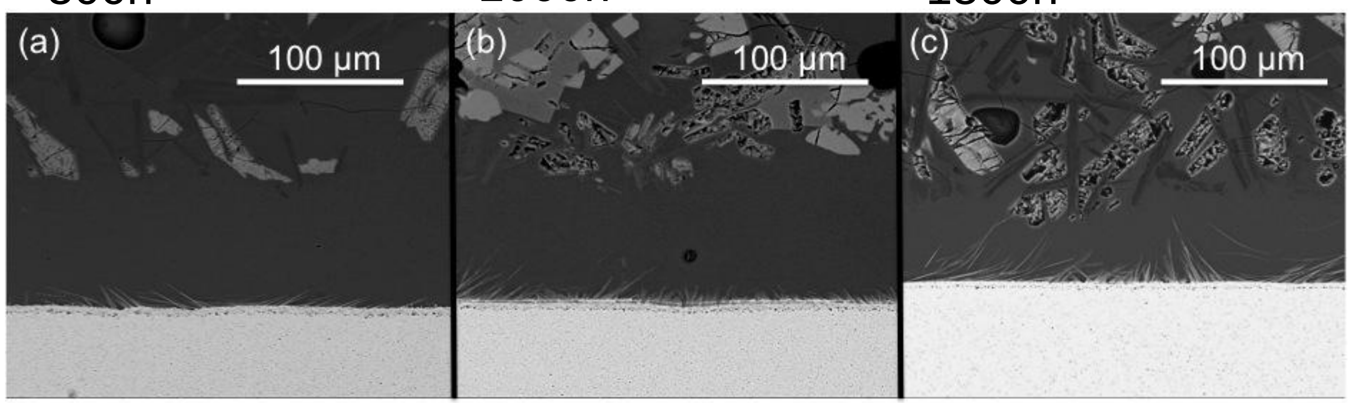
Low alkali boro-gallio-silicates on 8YSZ at 850 C in air

500h 1000h 1500h



- Amorphous interface with 8YSZ up to 1500h

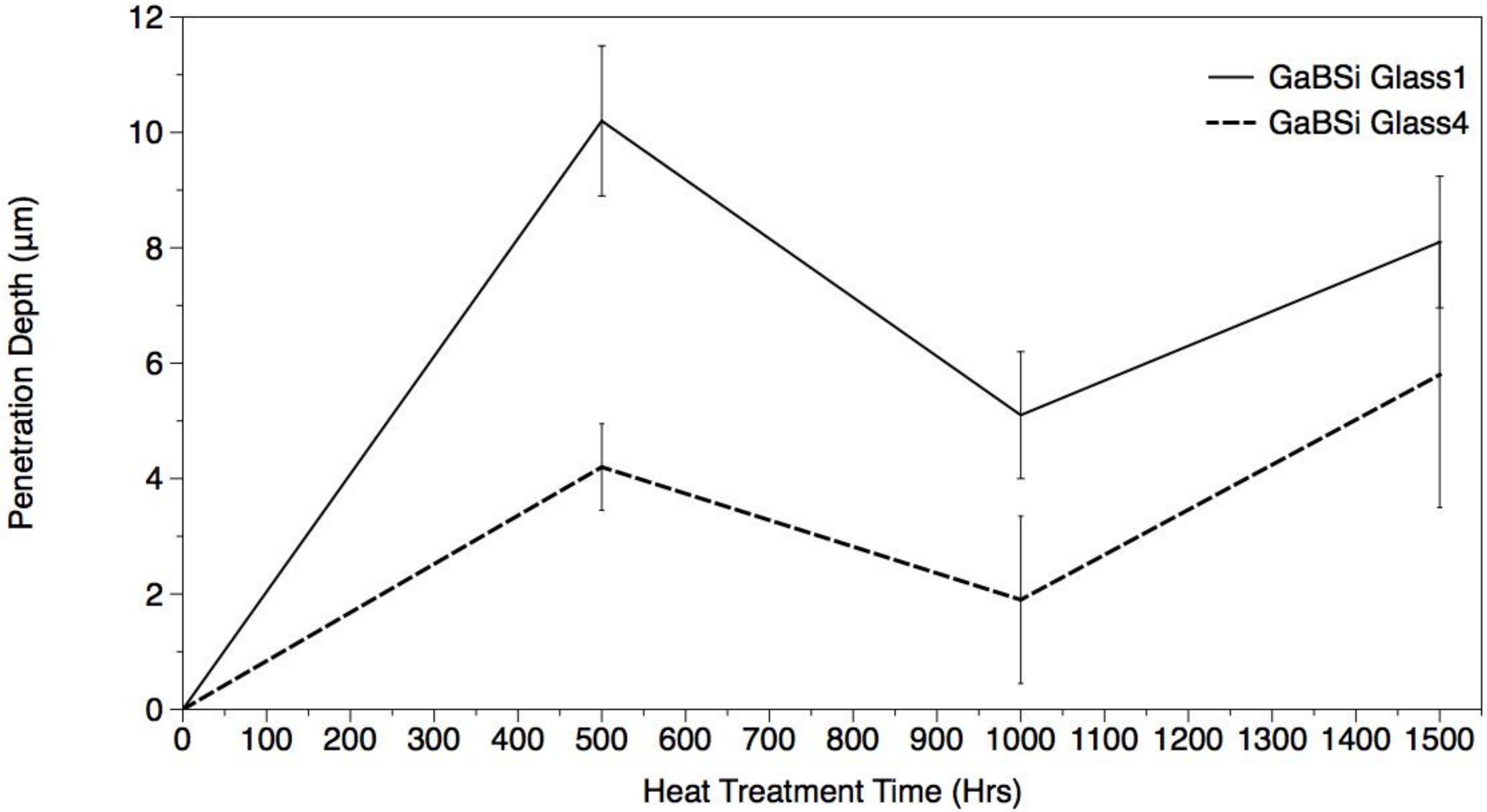
500h 1000h 1500h



- Partially crystallized interface with 8YSZ after 1000h

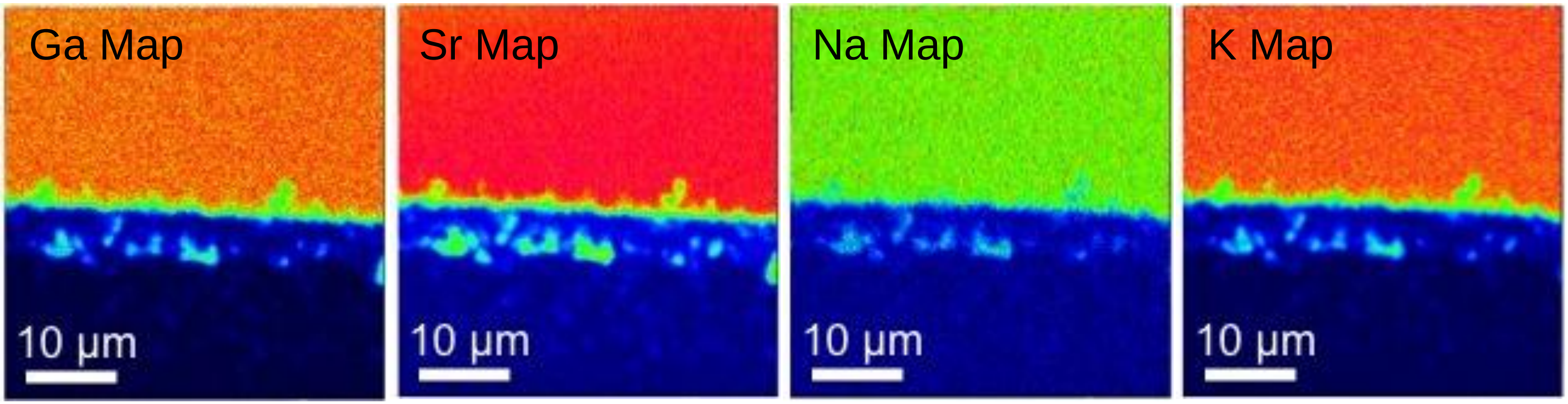
Interactions with 8YSZ Substrates

Reaction zone with 8YSZ up to1500h at 850 C: within ≈10μm of original surface

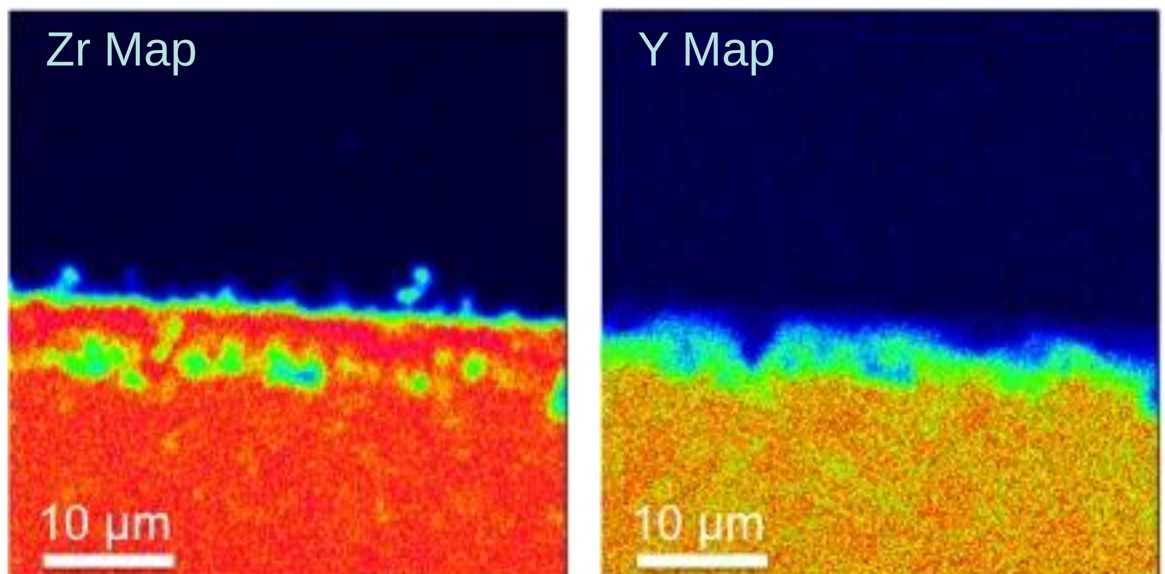


Chemistry at the 8YSZ Interface – 500h

Diffusion of glass components via grain boundaries into the 8YSZ after 500h at 850 C

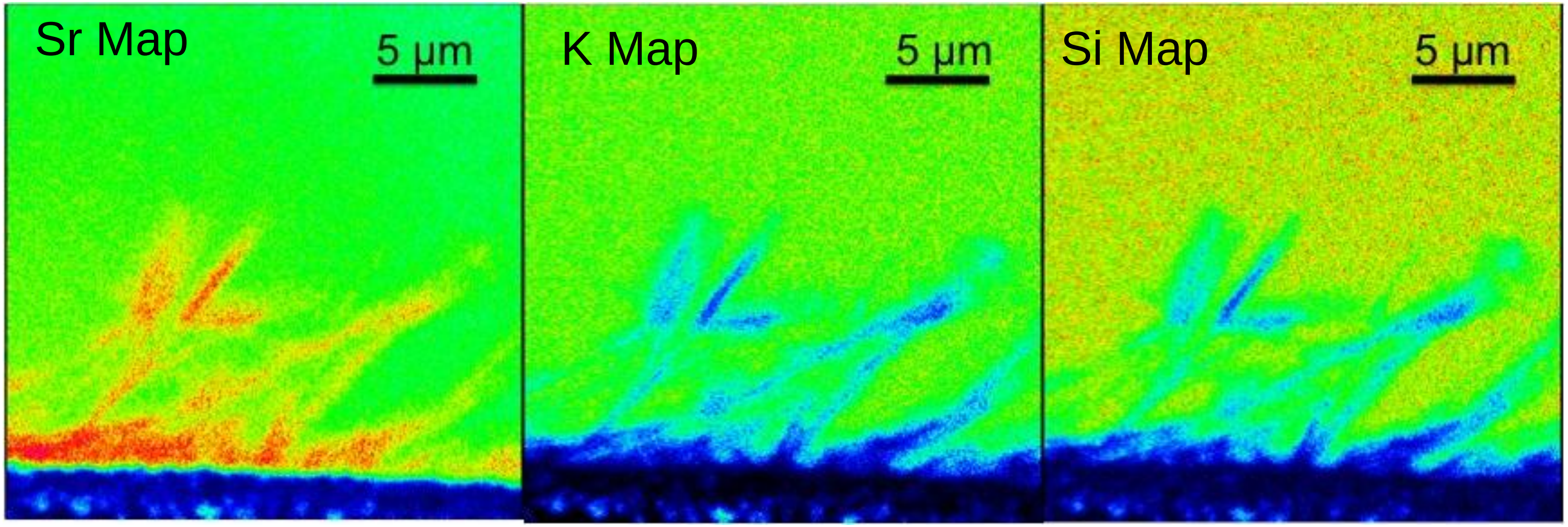


Y ions react with or diffuse into the glass more readily than Zr ions.



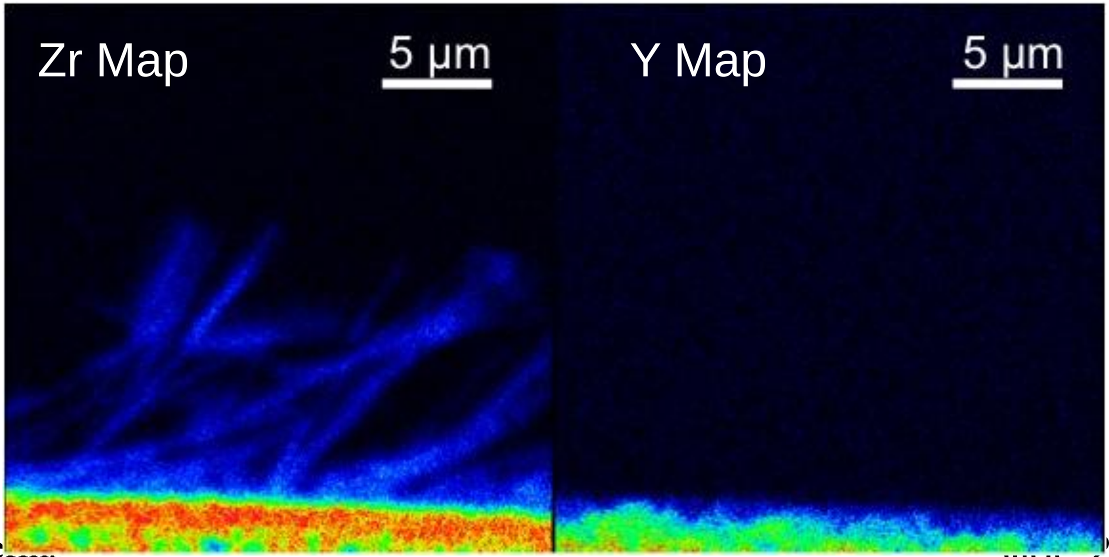
Interfacial reaction yields crystals – 1500h

Interfacial crystallization at the 8YSZ interface after 1500h at 850 C



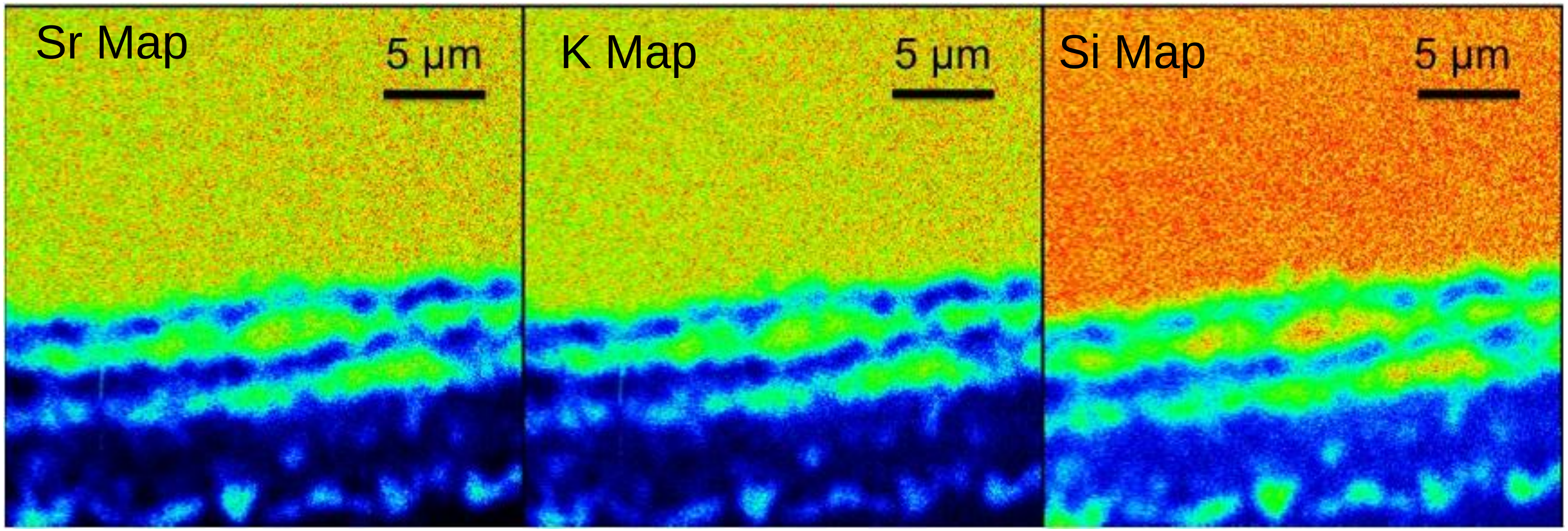
Interfacial crystals:

$SrZrO_3$

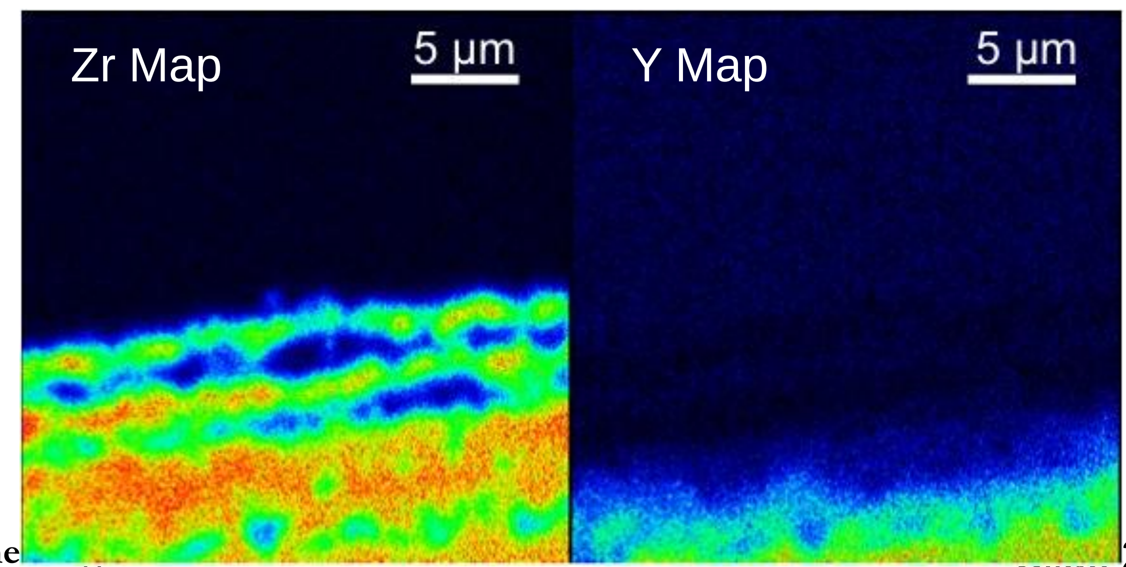


Change glass composition to inhibit crystallization

Microprobe maps of glass-8YSZ interface after 1500h at 850 C

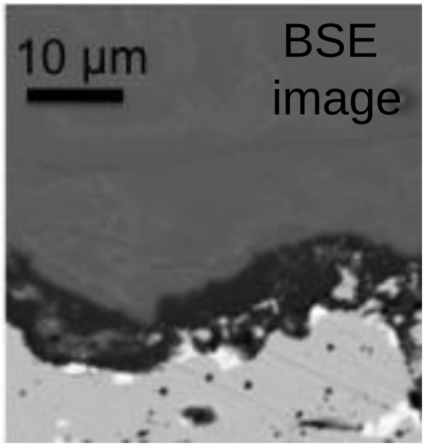


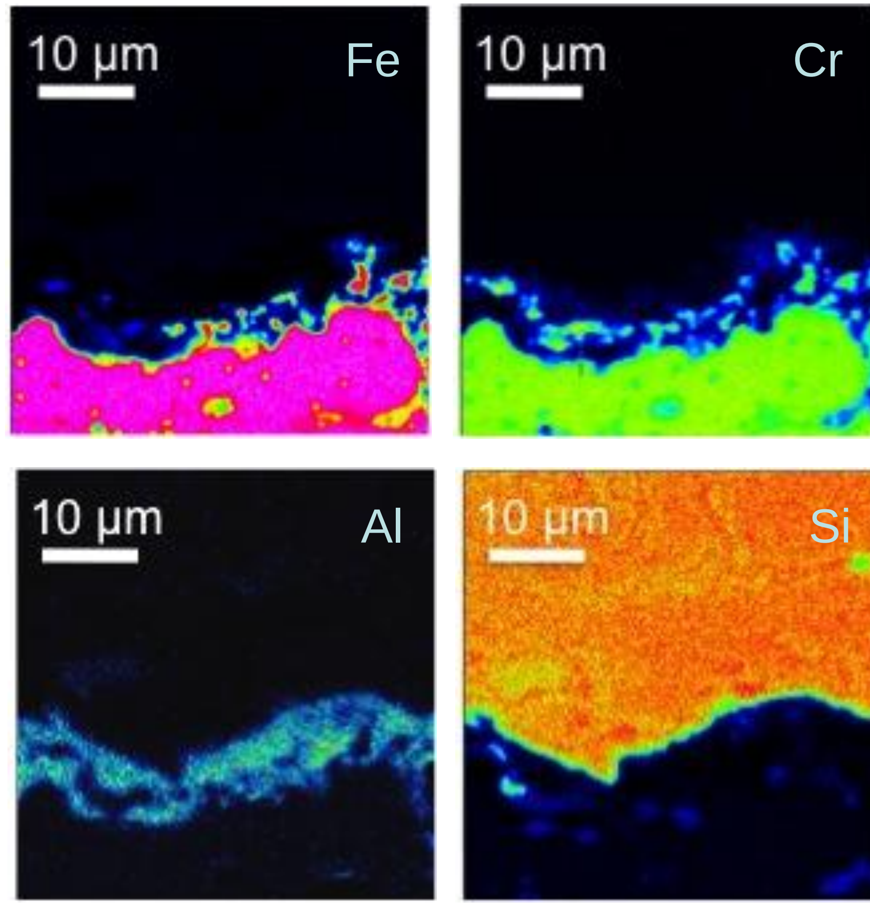
Reaction zone into YSZ along interface



Interactions with Aluminized Stainless Steels

Interface of a GaBSi2 glass with Al-441SS substrate after 500h at 850 C
- SS substrate on bottom of image

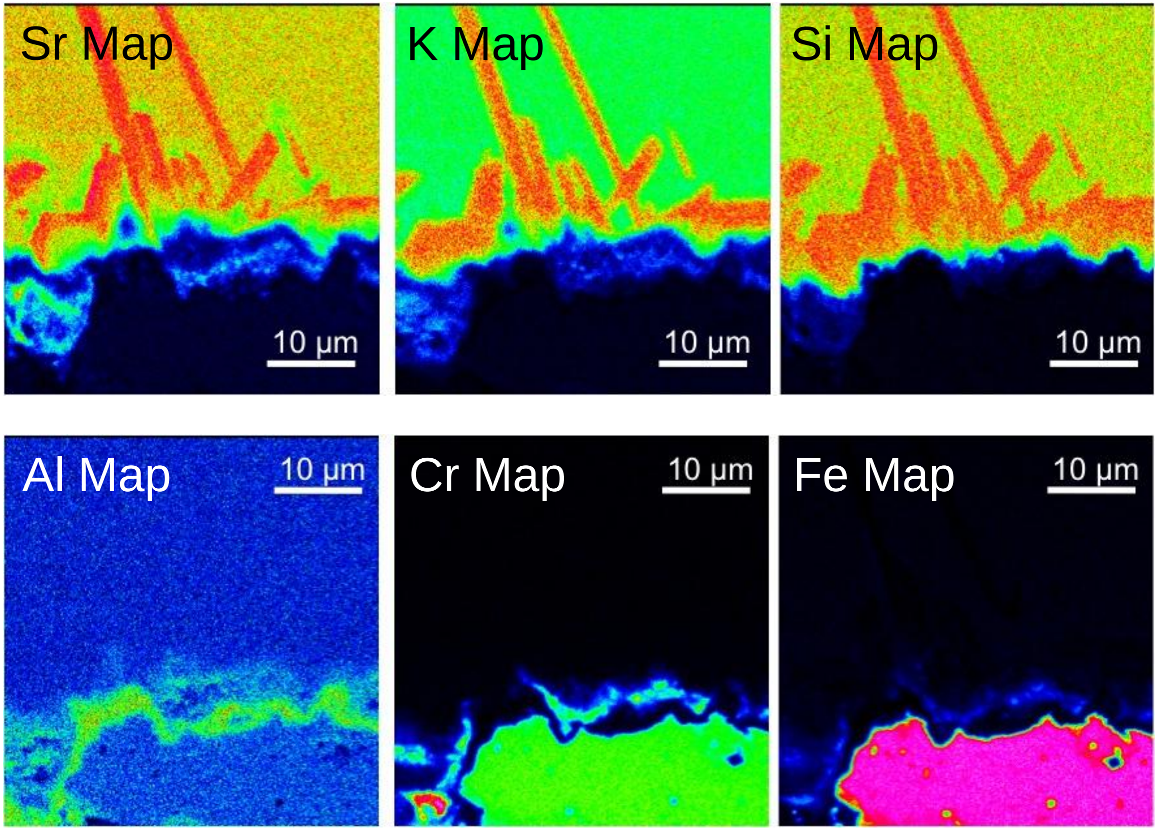




1. alumina coating remains after 500h
2. coating impedes diffusion of chromium and iron ions into the glass

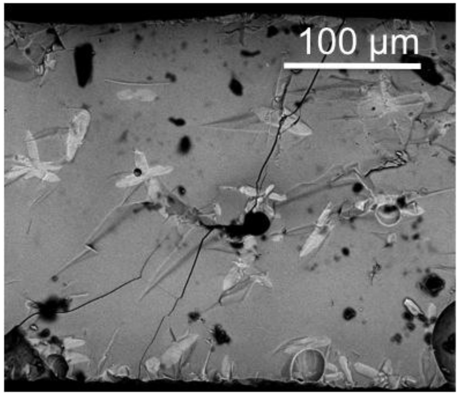
Generally Find Crystallization at the Al_2O_3 Interface

Interfacial crystallization of a GaBSi2 glass with Al-441SS substrate after 500h at 850 C

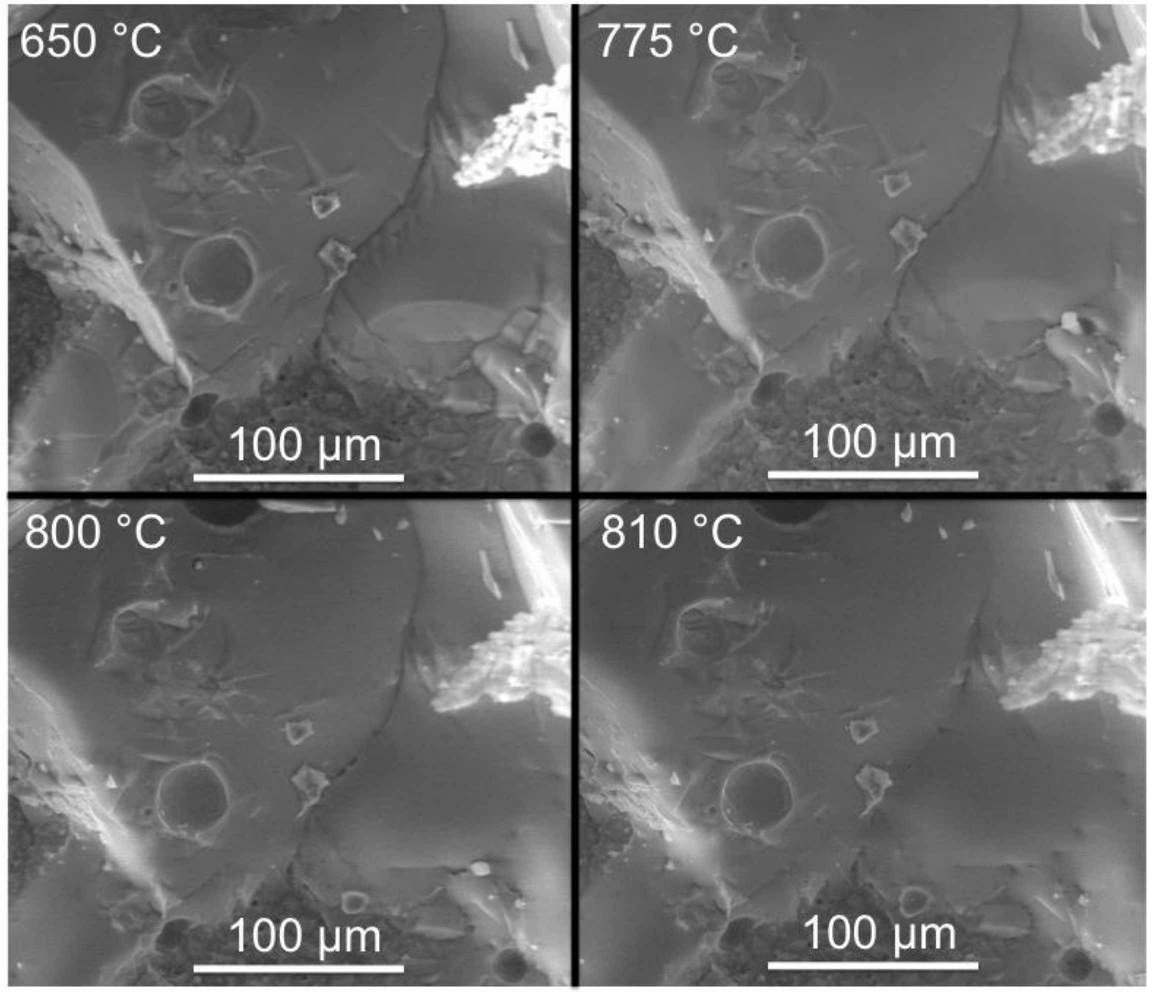


Crystals are $KSrSiO_6$

Boro-Gallio-Silicates – Direct Observation of Crack Viscous Sealing



In-situ high temperature SEM



Initial Search for Germanate 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

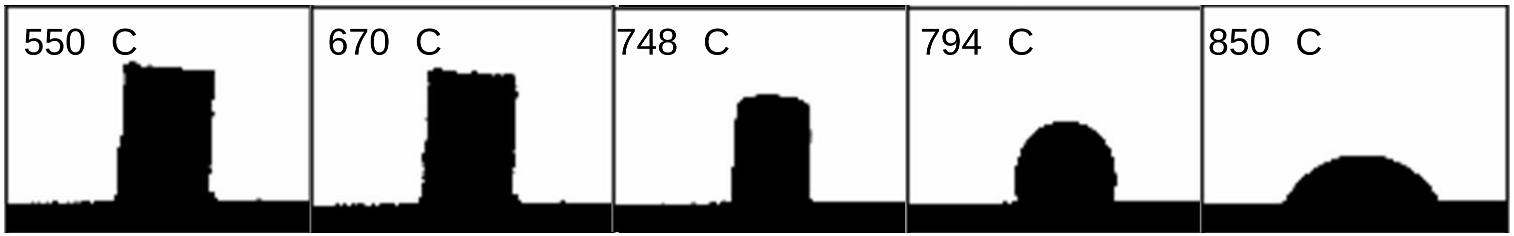
3rd Optimization: B-Ge-Si-O Glasses

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

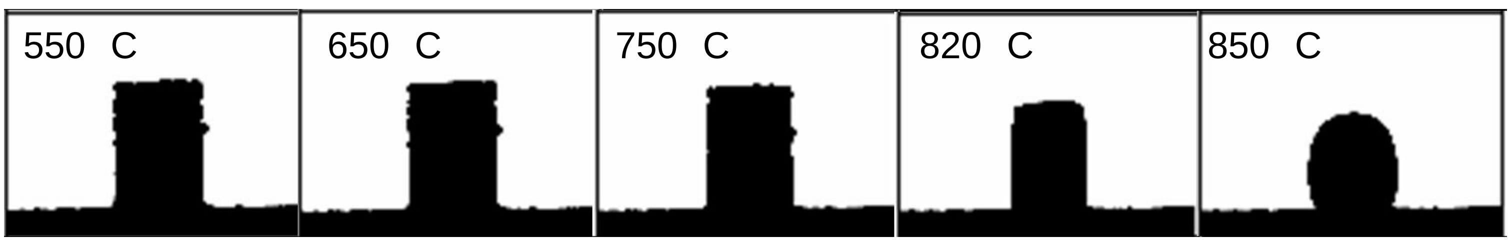
Glass Series	Alkali (mol %)	B_2O_3 (mol %)	Tg (C)	CTE (ppm/K) (100-400 C)
High Temp	20	<10	590 - 770	9 - 12
BGeSi	10	<10	540 - 590	7.5 - 10
BGeSi2	5	<10	610 - 640	8 -9

BGeSi Flow to 850C

Press <50 µm glass powder into 3 mm pellet
Heat furnace at 5 C/min



BGeSi glass: excellent flow before 850 C
significant flow by 750 C

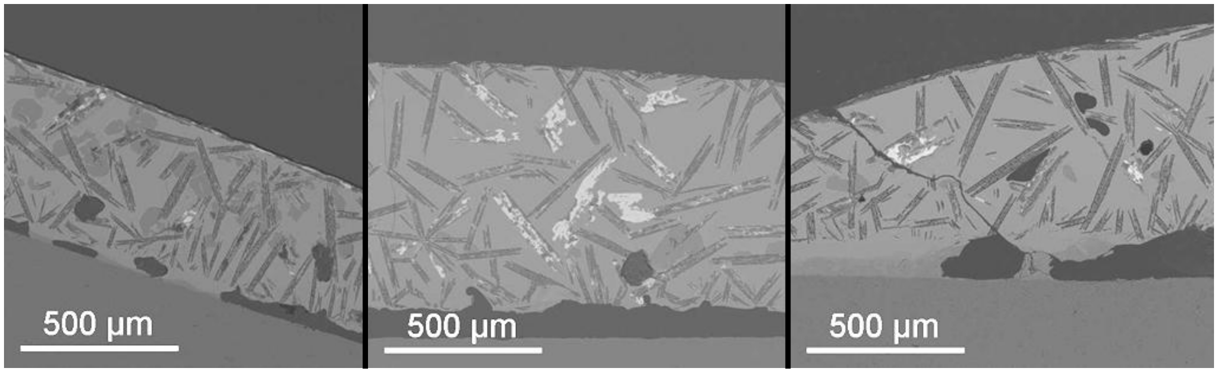


BGeSi glass (non-alkali): significant flow before 850 C

Maintained desirable flow with non-alkali BGeSi glasses

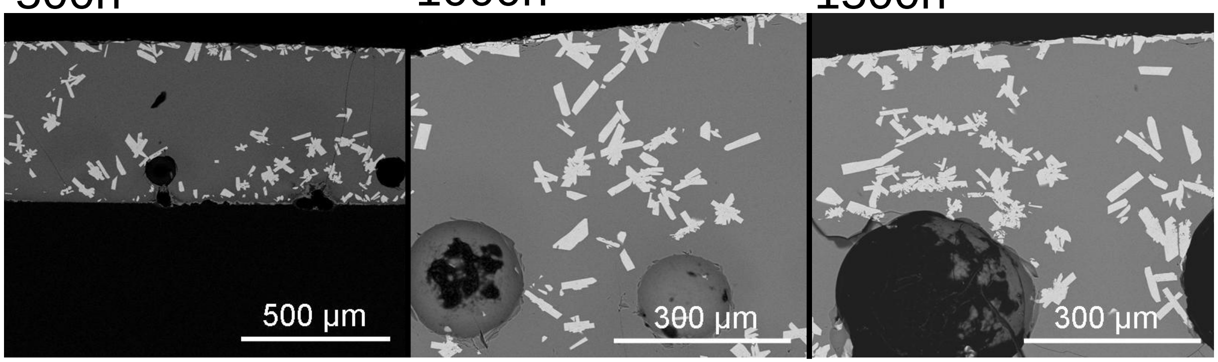
B-Ge-Si-O on Al_2O_3 retain ~70% amorphous phase after 1500h at 850°C

500h 1000h 1500h



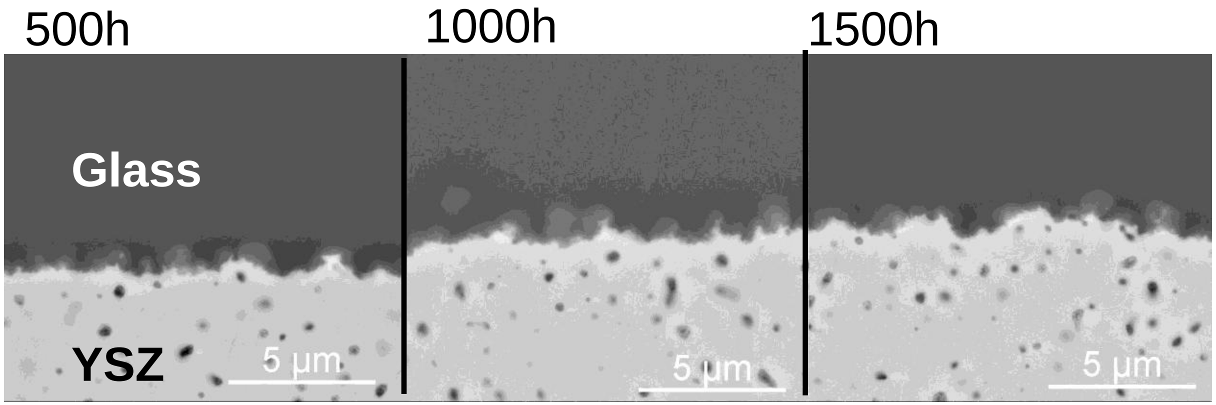
Extensive crystallization at interface

500h 1000h 1500h

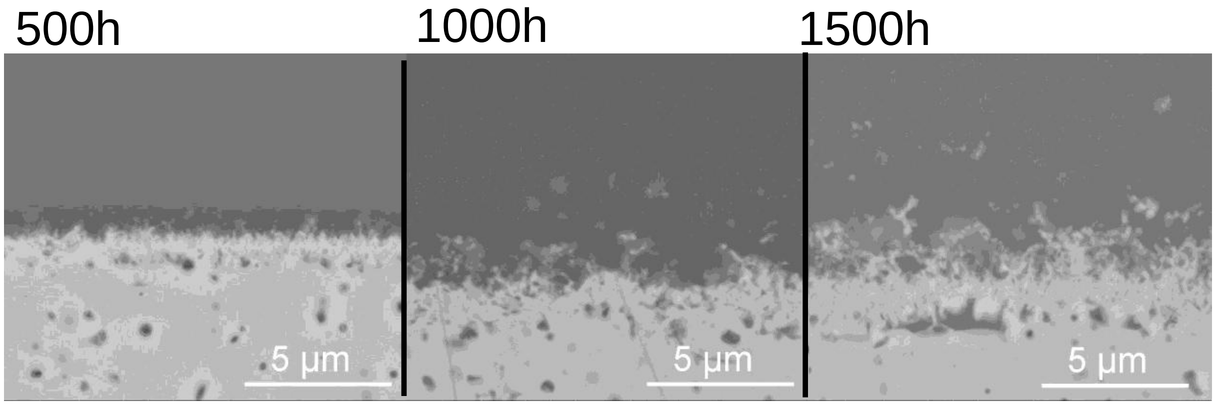


Largely amorphous interface

Interaction with YSZ Depends on Chemistry



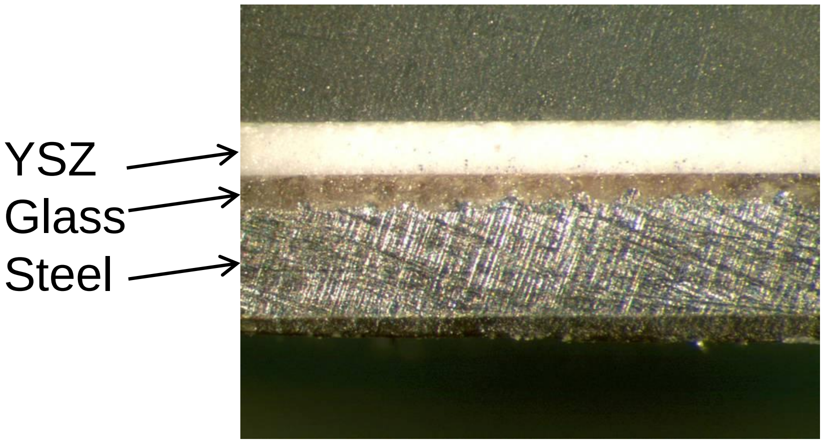
No attack of YSZ

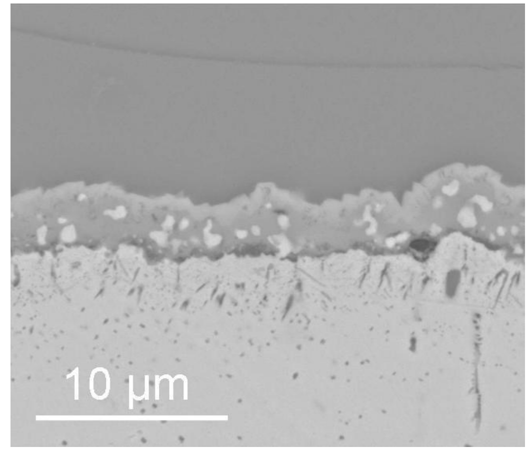


Slow dissolution of YSZ

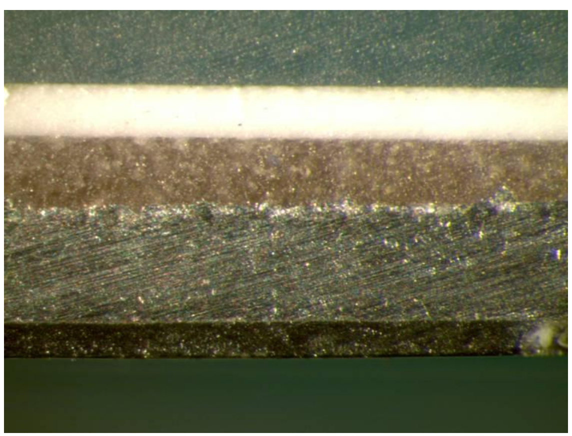
Test Seals: Aluminized SS vs. 8YSZ

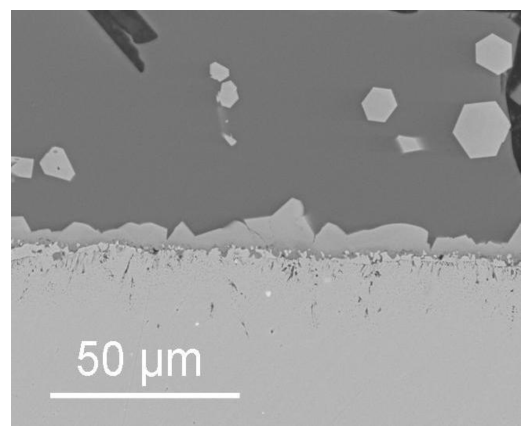
Stable on cooling from 500h at 850 C



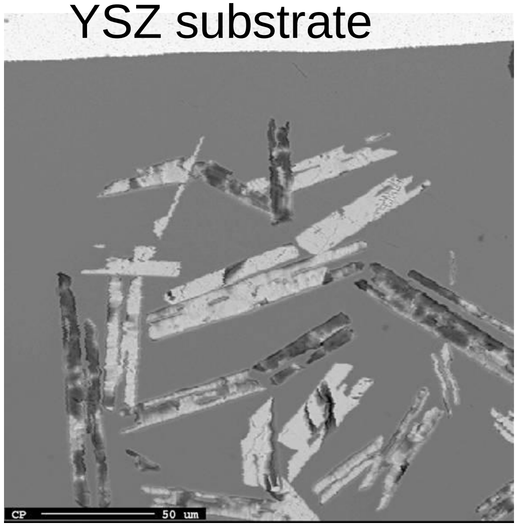


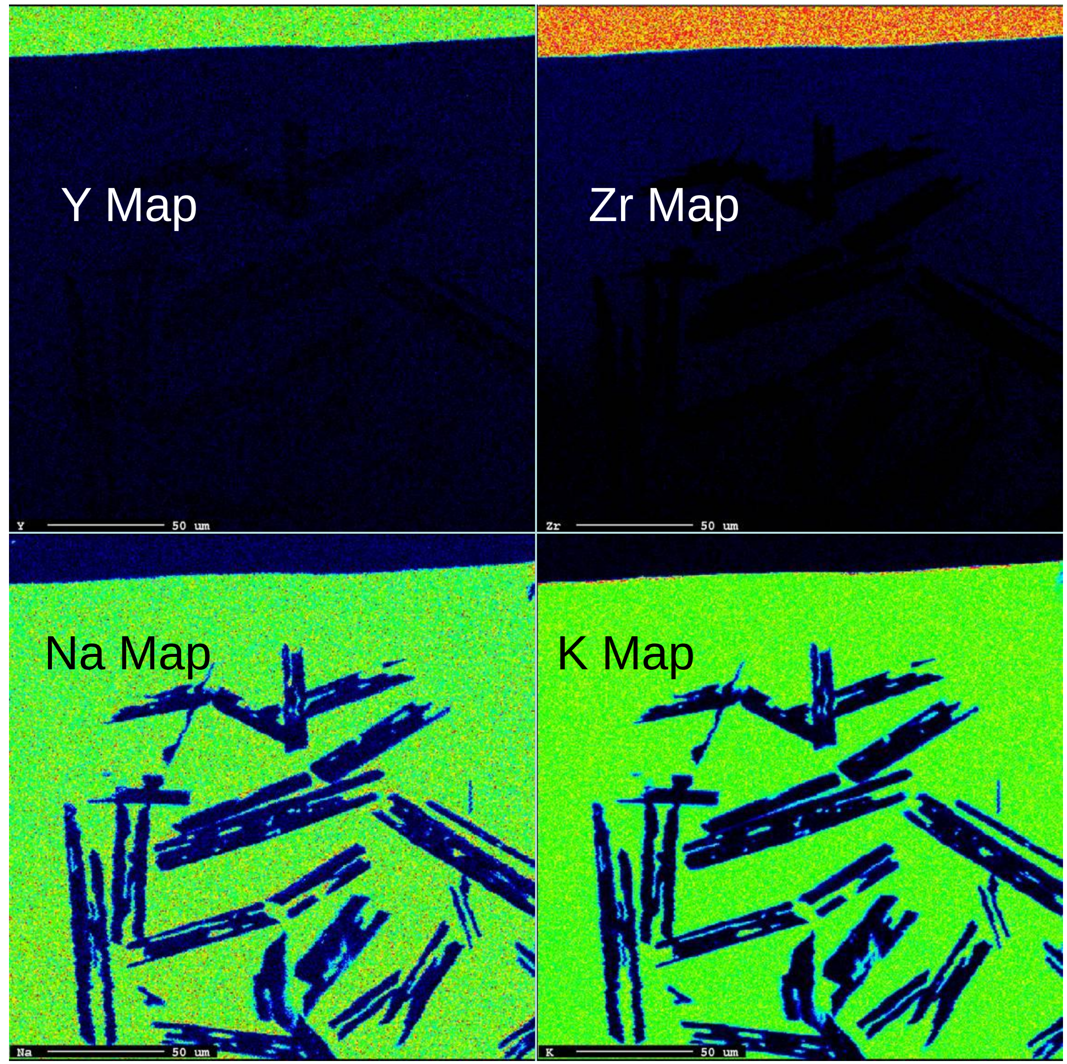
Crystals at SS/glass interface are stable.





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

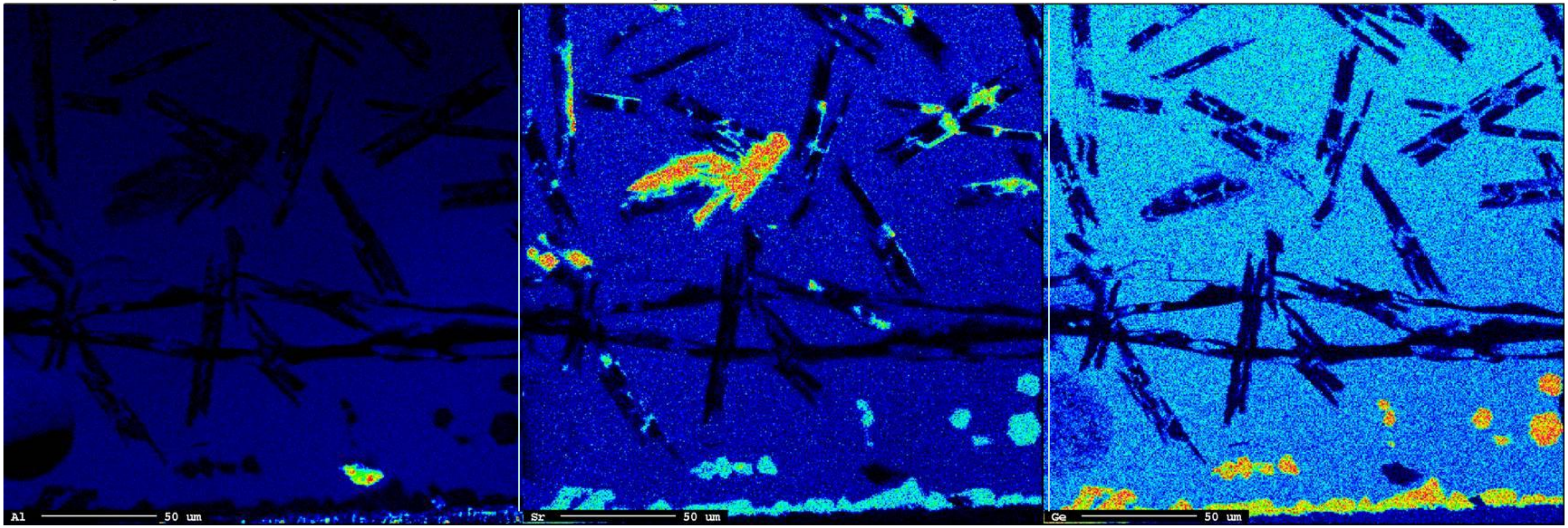




- no preferential diffusion of alkali
- minimal diffusion of Zr and Y into the glass

Some Attack of Al_2O_3 Layer Possible, Depends on Composition

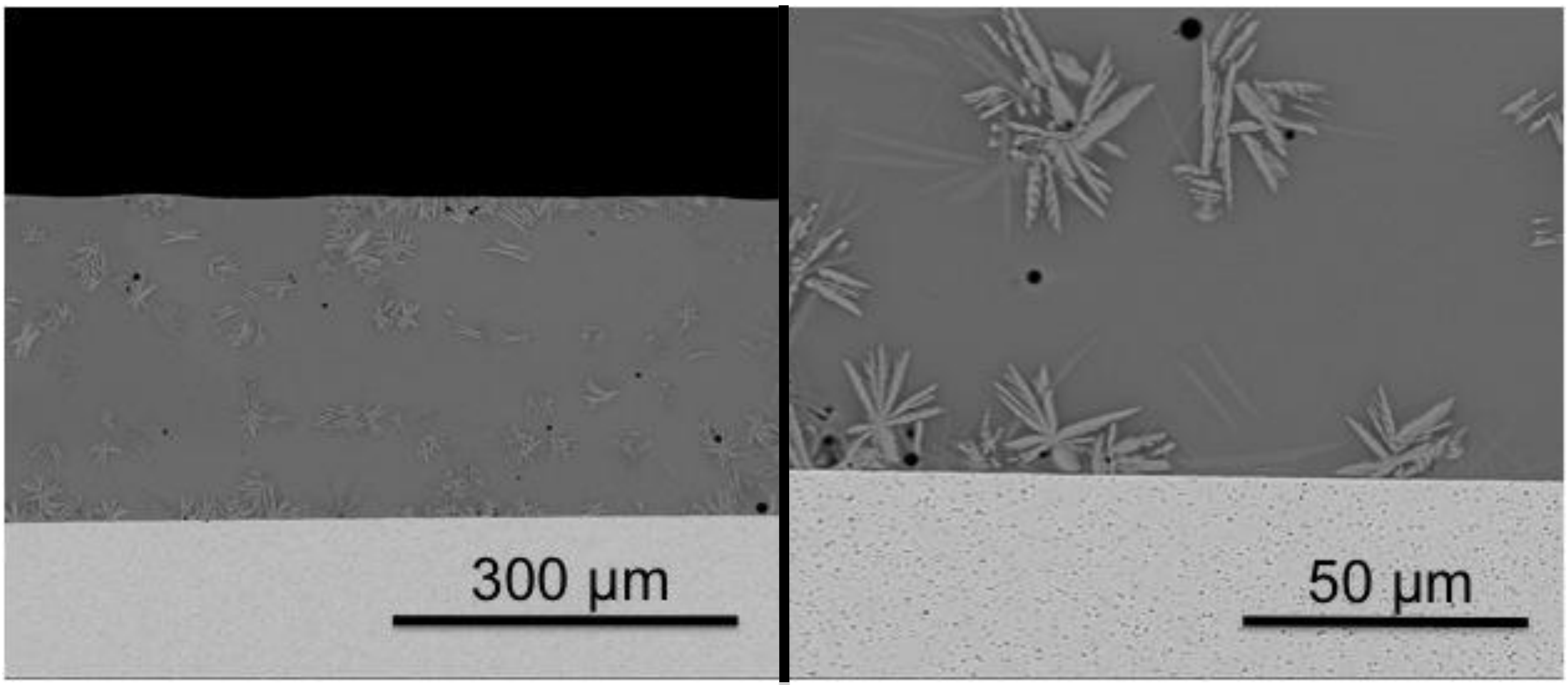
Al map | Sr map | Ge map



Note Ge enrichment at interface – good or bad?

Low Reactivity with 8YSZ

- Non-alkali BGeSi glass does not dissolve the electrolyte: 500h at 750 C
  - Only bulk crystallization



Summary

Identified potential new glass compositions to enable viscous sealing

- Modified gallio-silicate glass compositions – low alkali & non-alkali
  - Optimized viscosity for sealing <850 °C
  - Identified possible OT ranges, which are defined by partial crysallization
  - Acceptable behavior when in contact with SOFC stack components after 1500h

- Modified germano-silicate glass compositions
  - Optimized viscosity for sealing at 650 °C and above
  - Studied crystallization behavior – best viscosity for sealing
  - Verified compatibility with SOFC stack components to 1500h

Acknowledgments

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- Joe Stoffa and Briggs White for guidance throughout
- Jeff Stevenson at PNNL for providing coated stainless steel samples