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. 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

3. Boro-germano-silicates seal between 650 and 850 °C
    1. Best thermomechanical match with SOFC stack components

4. New glasses from remnant glasses in (2) do not bulk crystallize

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 glass phase allows flow

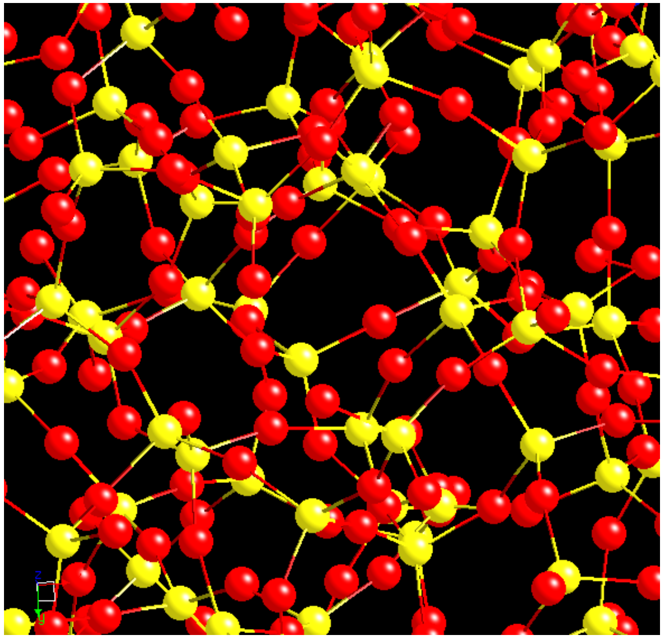
  Crystals may reduce mass transport through the glass & prevent degradation over time

  Crystals may improve mechanical behavior

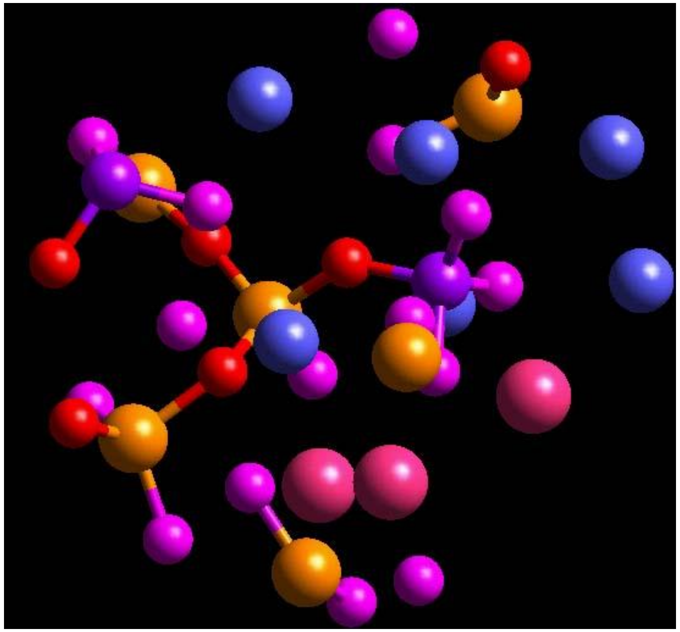
Overall Glass Composition Strategy

Maintain a high concentration of glass former

a) achieve controlled viscosity behavior
b) minimize crystallization



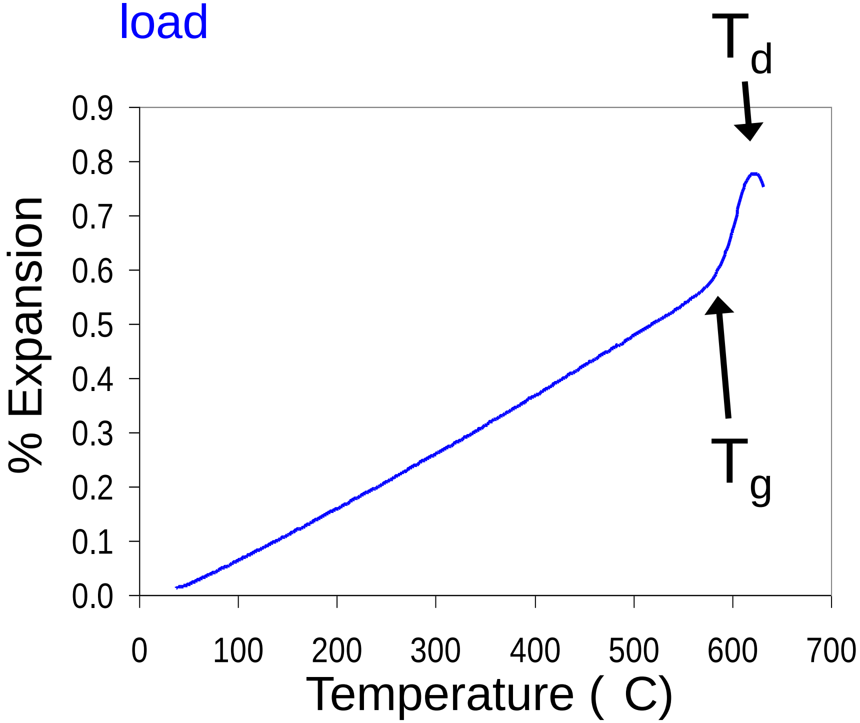
Vitreous network
- Controlled viscosity

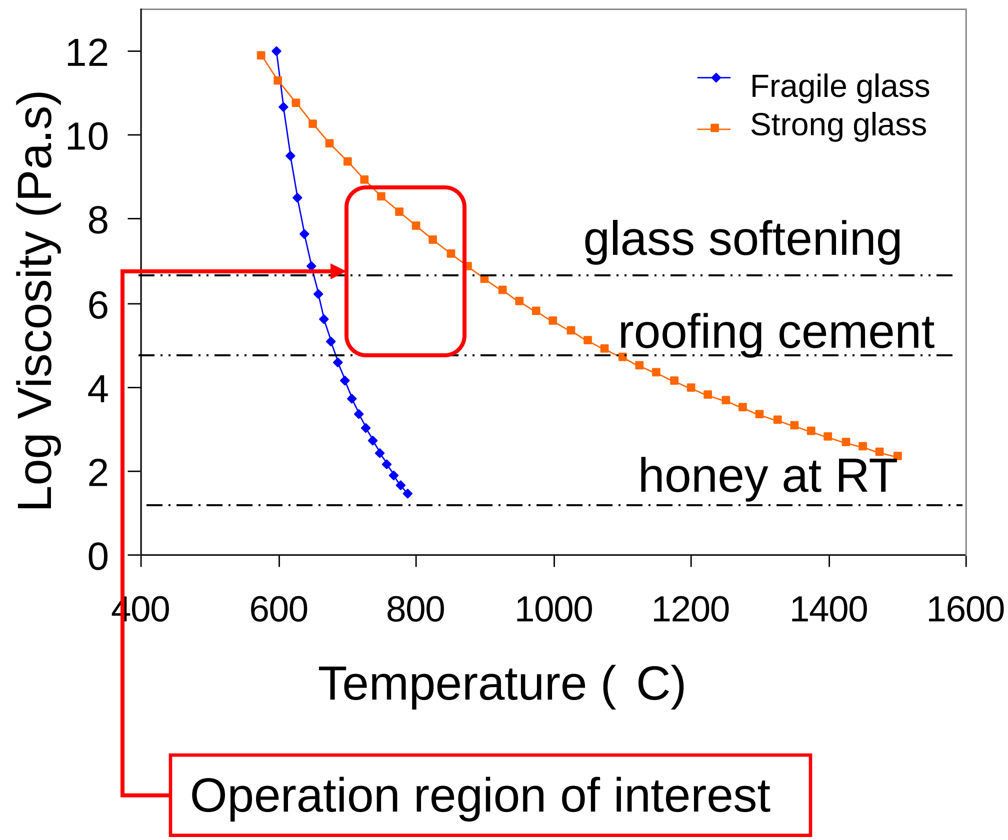


Inverted structure
- Fragile viscosity
- Crystallization

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
  - higher CTE, lower Tm than SiO_2,
  - greater chemical durability than borate glasses
  - allows lower Tg

- 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

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)	T_{seal} (C)
High Temp	20	<10	590 - 770	9 - 12	> 950
GaSi	10	<10	640 - 650	9 - 10	≈ 900
GaBA	5	<10	610 - 630	7 - 10	≈ 850
GaSiB	0	<10	650 - 670	8 - 10	≈ 750

Encouraging results:

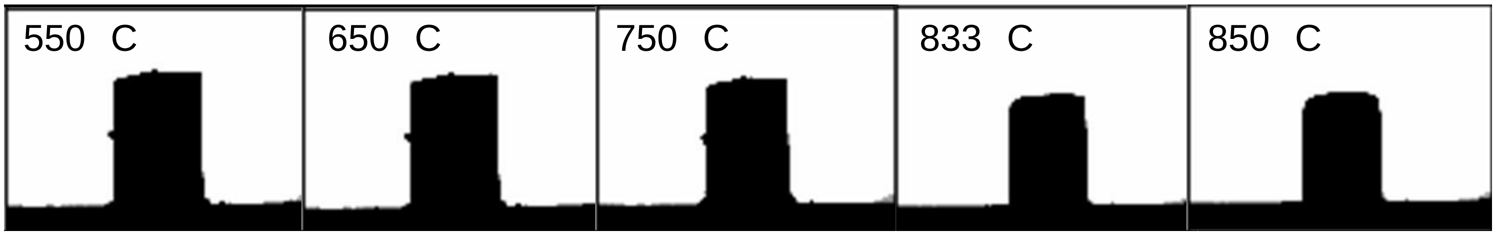
- T_{seal} decreases with decreasing alkali content
- Tg approaches 600 C with only 5 mol% alkali

GaBA and GaSiB series show the appropriate T_{seal} range

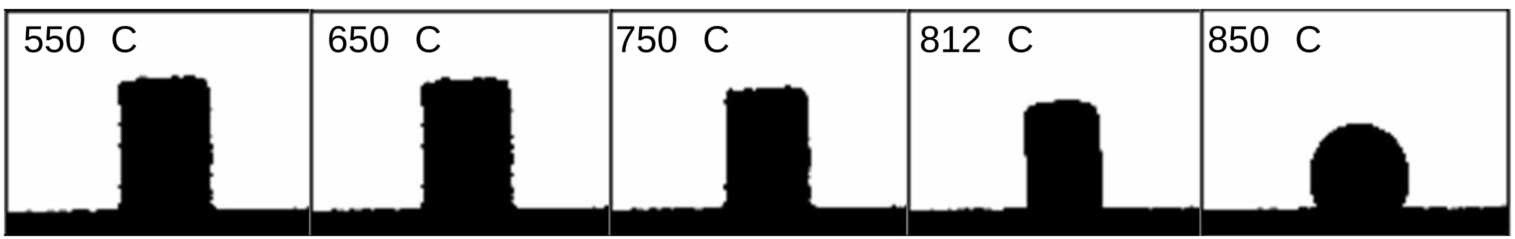
Additions of Boron to Improve Flow Behavior

Hot Stage Microscopy:

Press <50 µm glass powder into 3 mm pellet



GaSi glass: no significant flow before 850 C

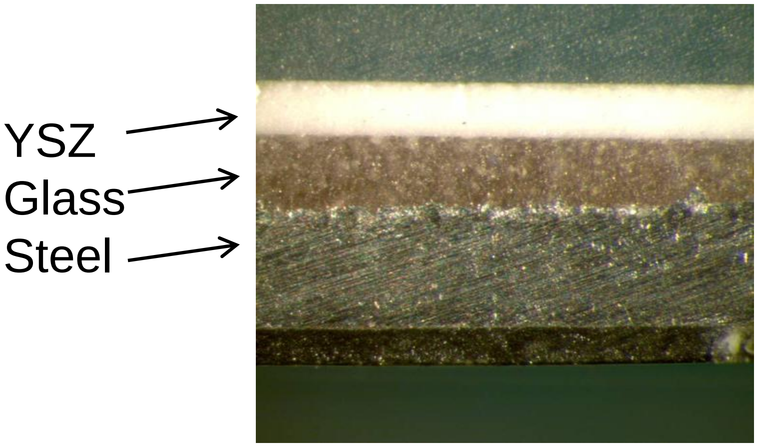


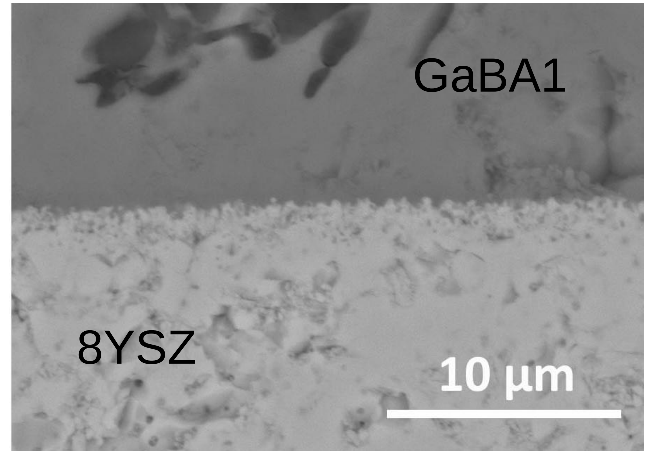
GaSiB glass: significant flow before 850 C

Achieved improved flow with non-alkali GaSiB glasses

Test Seals: Stainless Steel vs. 8YSZ

Glass samples are sandwiched between 8YSZ and Al-SS

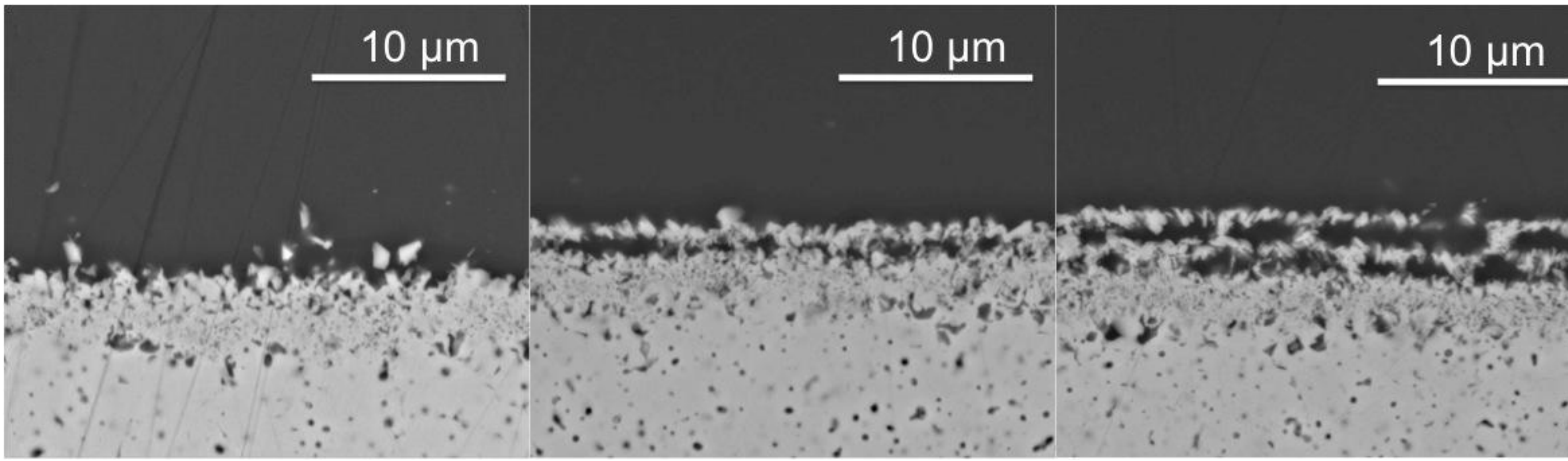




8YSZ Generally Inhibits Interfacial Crystallization

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

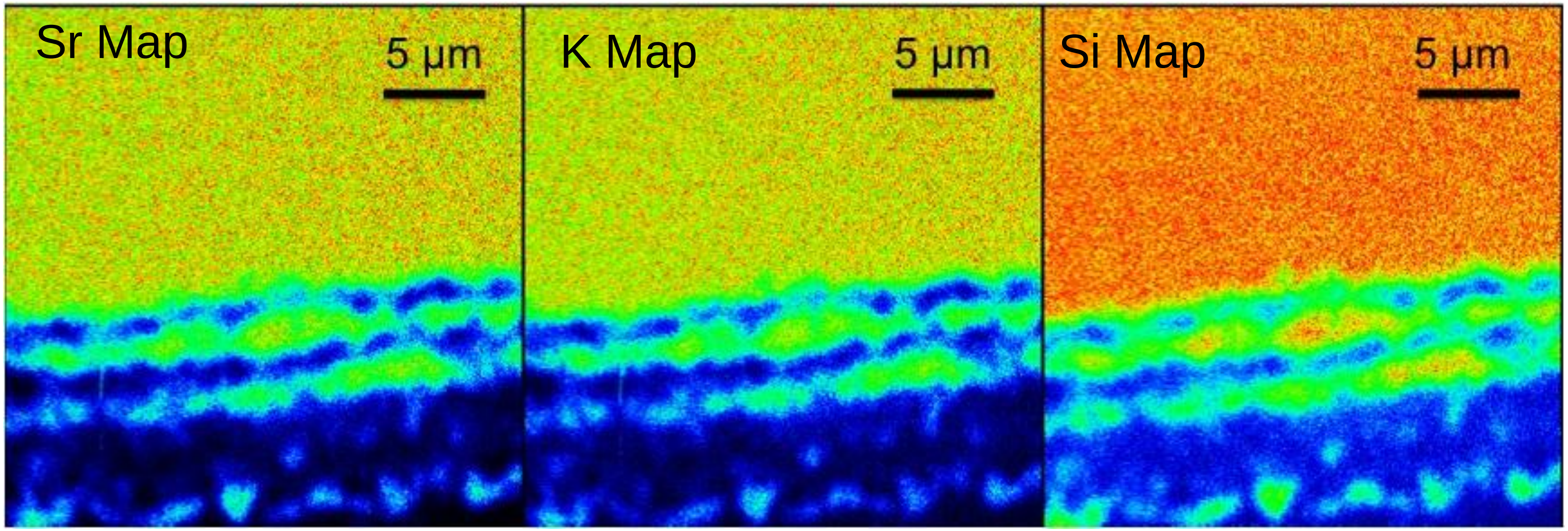
500h 1000h 1500h



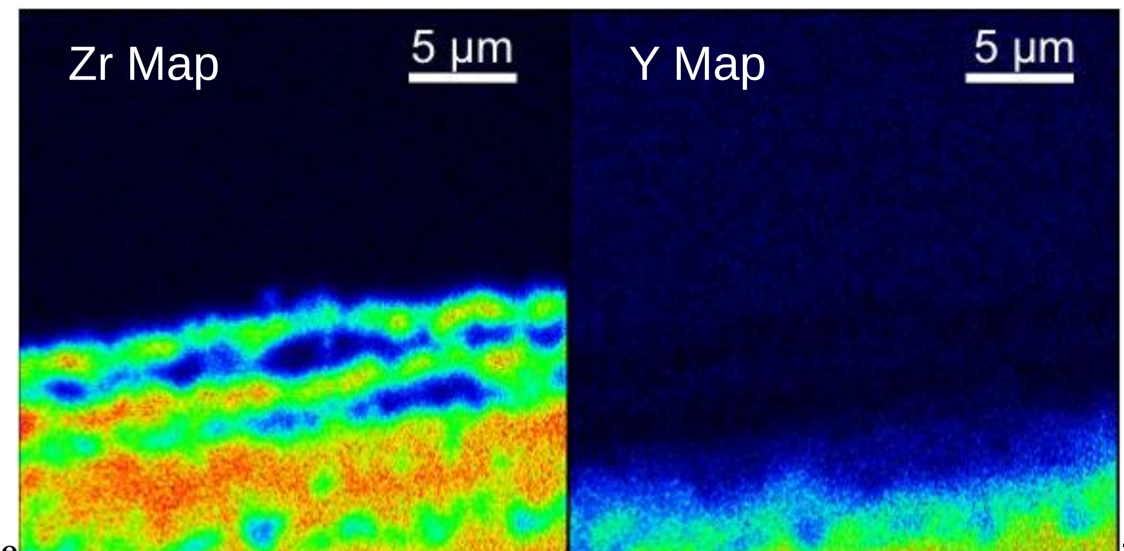
- Amorphous interface with 8YSZ up to 1500h

Glass composition determines crystallization

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

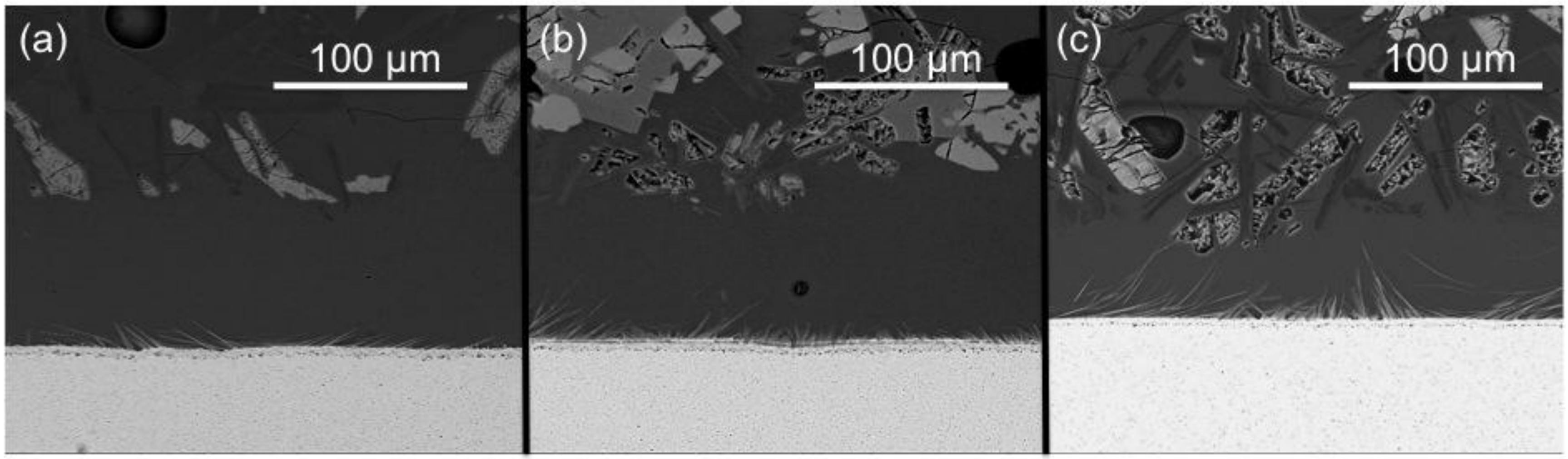


Reaction zone into YSZ along interface



8YSZ Generally Inhibits Crystallization – some glasses develop Sr zirconate crystals at YSZ interface

500h 1000h 1500h

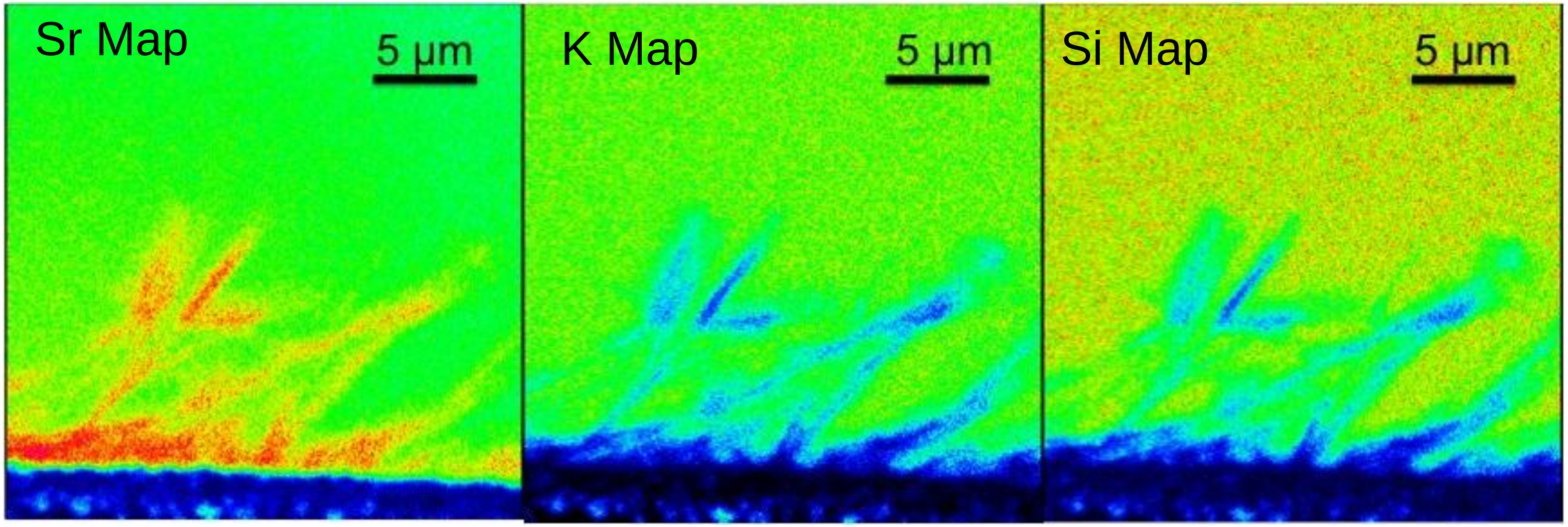


Low alkali boro-gallio-silicates on 8YSZ at 850 C in air

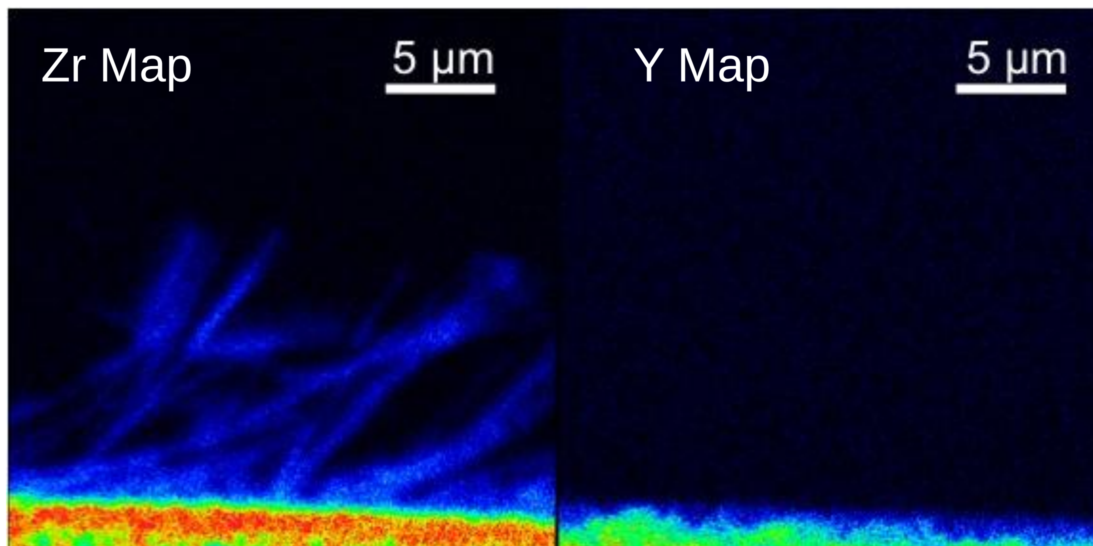
- Partially crystallized interface with 8YSZ after 1000h – DIFFERENT CRYSTALS THAN BULK

Interfacial reaction yields Sr zirconate crystals – 1500h

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

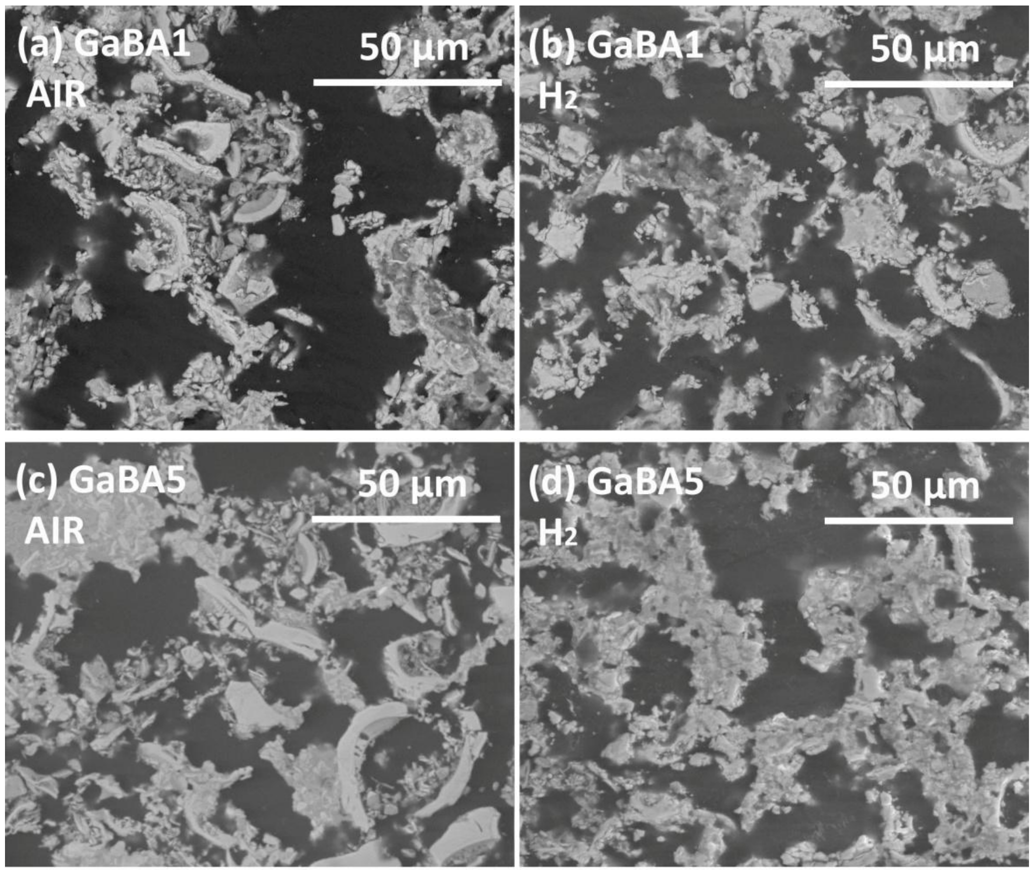


Interfacial crystals:
$SrZrO_3$



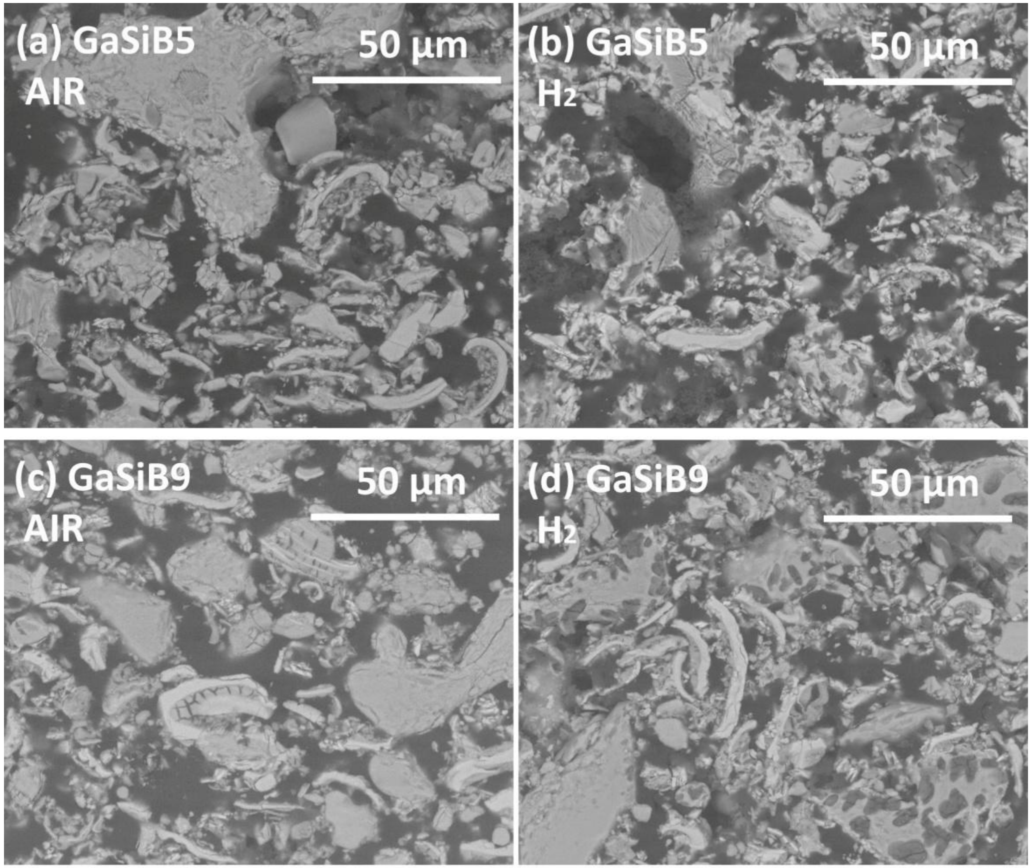
Alkali Boro-Gallio-Silicate (GaBA) Glasses – With YSZ in Dry Hydrogen

Glass powder mixed with 8-YSZ powder
Thermally treated for 100 hrs at 850 C



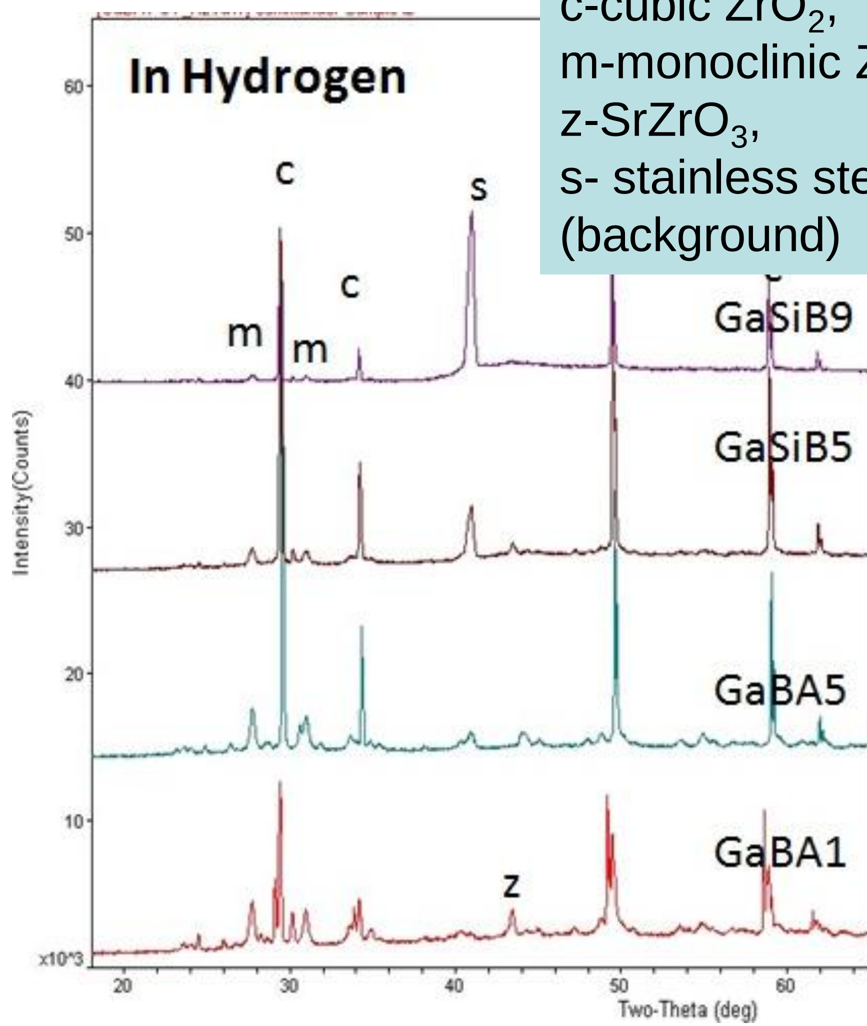
Alkali Boro-Gallio-Silicate (GaSiB) Glasses – With YSZ in Dry 4% Hydrogen

Glass powder mixed with 8-YSZ powder
Thermally treated for 100 hrs at 750 C



See partial phase change in YSZ powder – clear evidence of the preferential dissolution of Y ions

- Glass powder mixed with 8-YSZ powder
- Thermally treated for 100 hrs in both air and 4% hydrogen

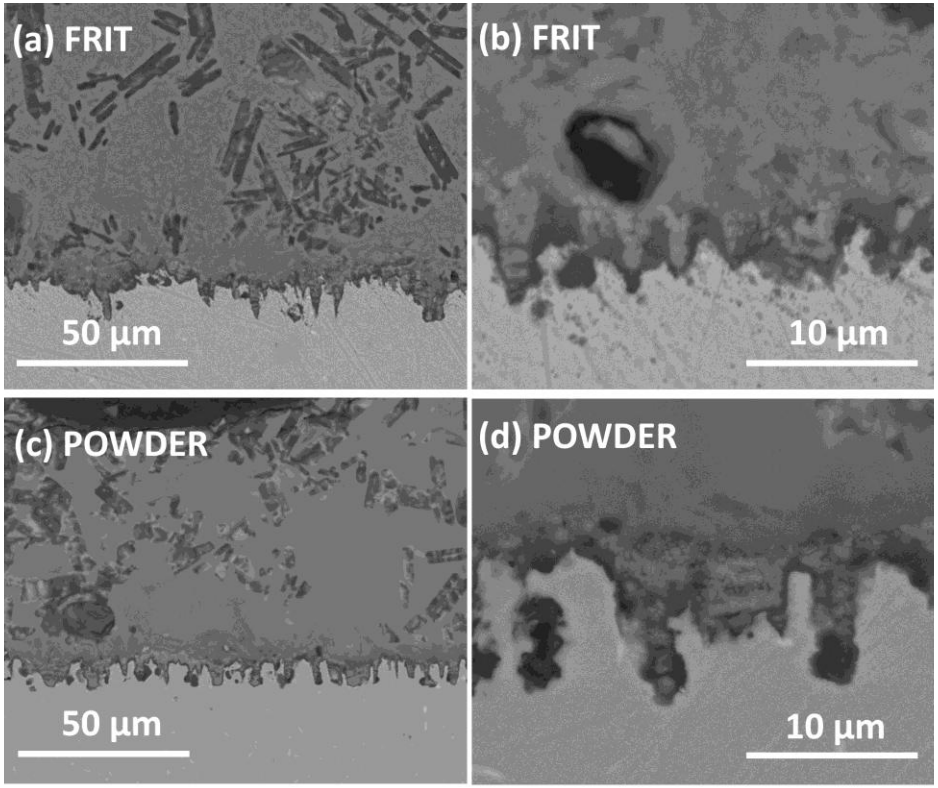


c-cubic ZrO_2,
m-monoclinic ZrO_2,
z-$SrZrO_3$,
s- stainless steel (background)

GaBA Glasses– No effect of glass powder particle size

- Frit (<53 μm) and powder (<220 μm) samples on Al coated stainless steel
- Crystallization for 100 hrs at 850 C
- High thermal stability of with large glassy content

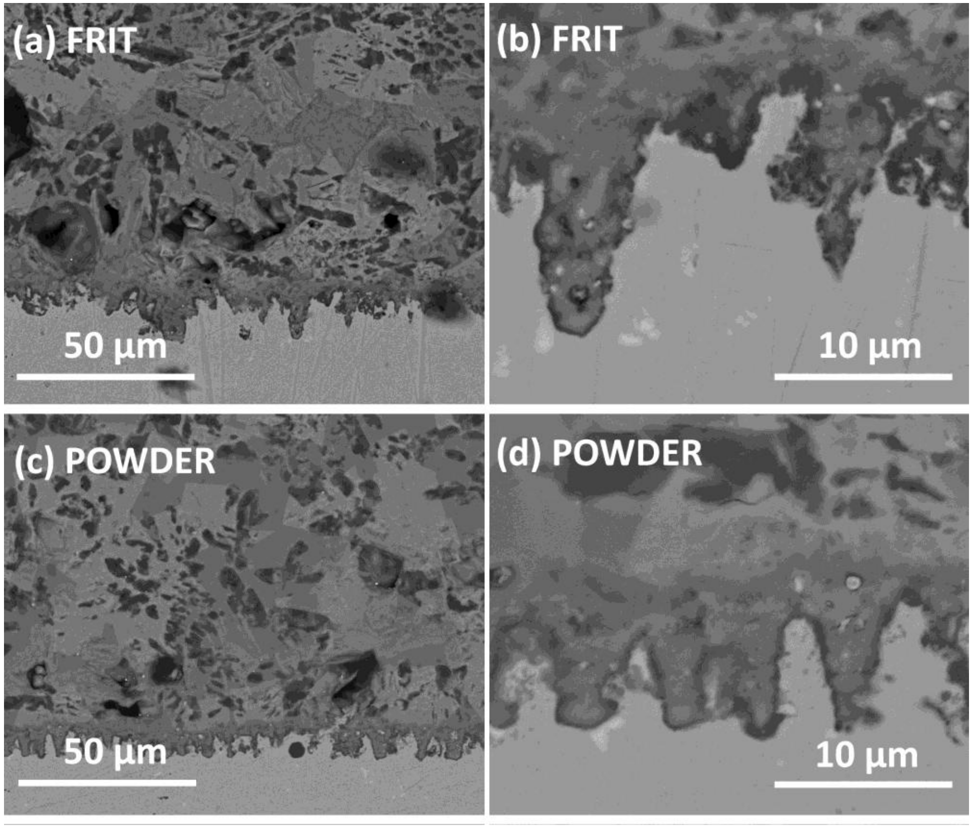
GaBA1 100 hrs



GaSiB Glasses – No Effect of Glass Powder Particle Size

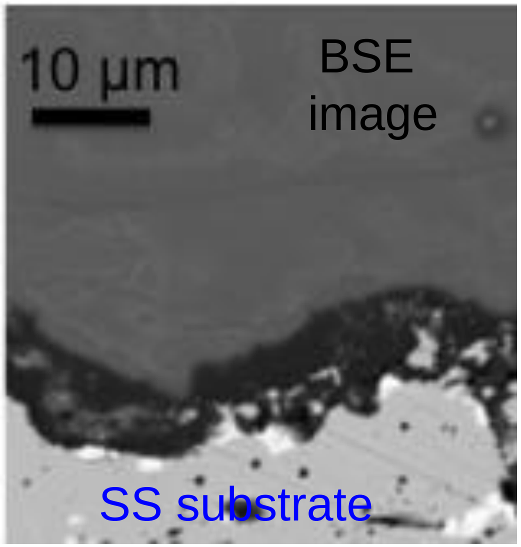
- Frit (<53 µm) and powder (<220 µm) samples on Al coated 441 stainless steel
- Extensive crystallization after 100 hrs at 850 C
- High thermal stability of microstructure, yet little remnant glass phase

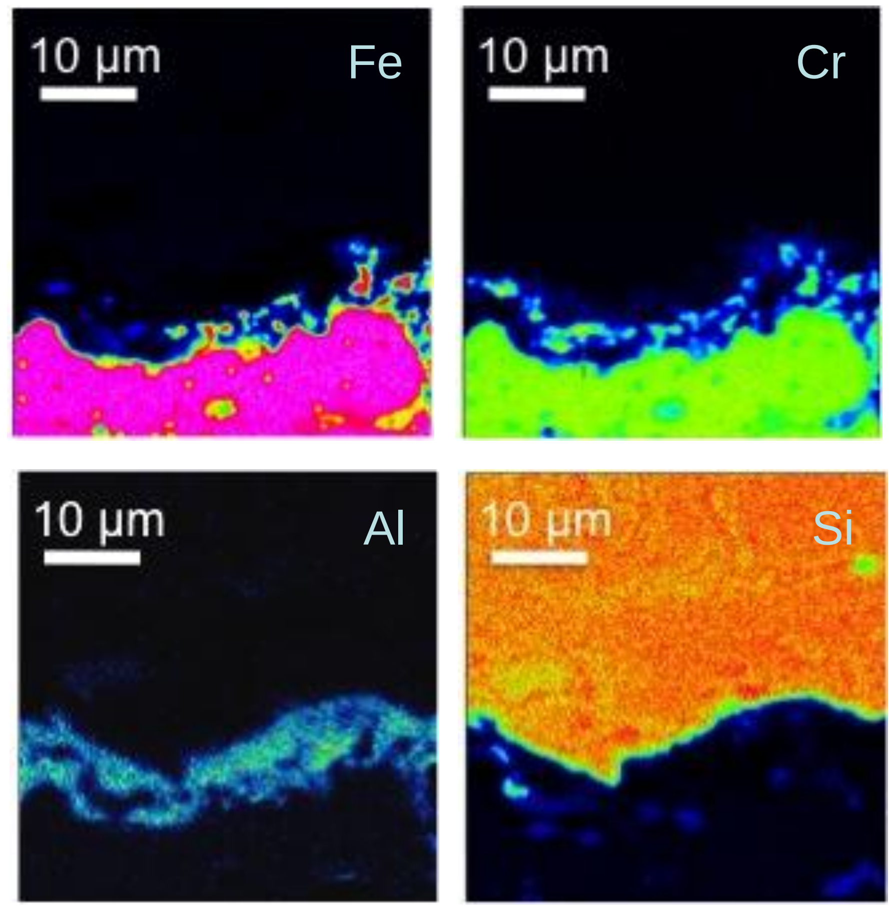
GaBA5 100 hrs



GaSiB Glasses with Aluminized Stainless Steel

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

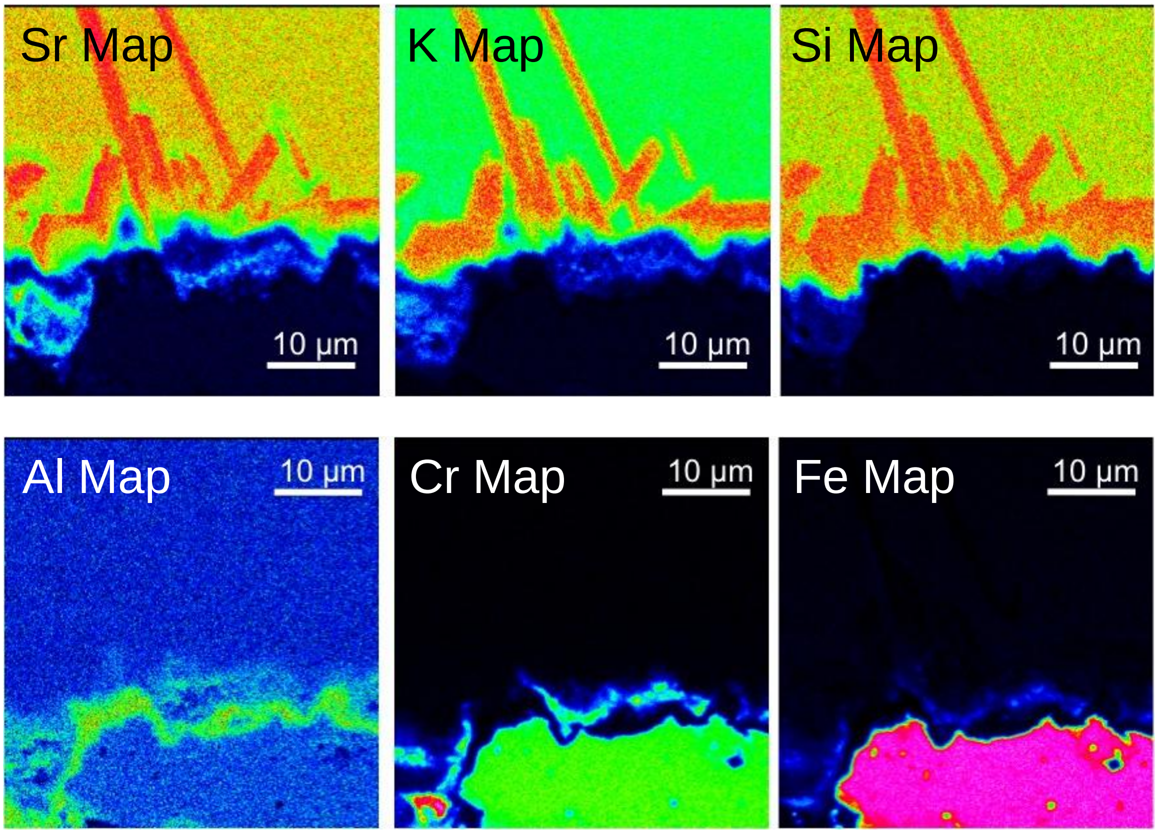




1. alumina coating remains after 500h
2. coating impedes diffusion of chromium and iron

Generally Find Crystallization at the Al_2O_3 Interface

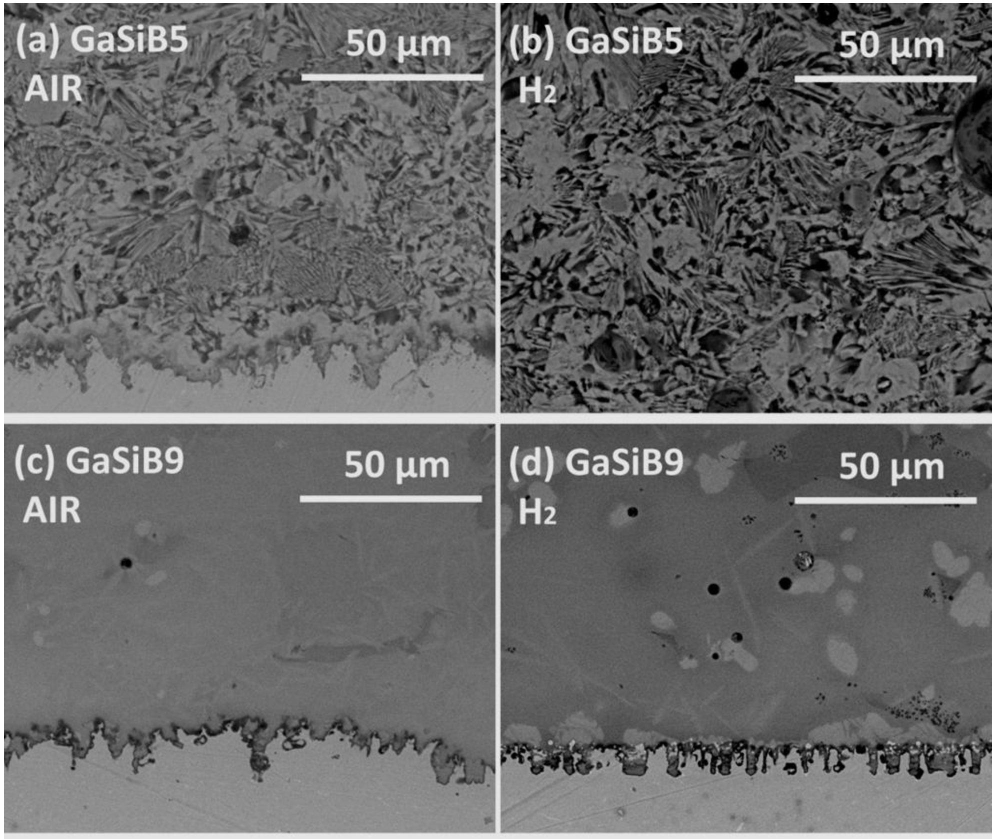
Interfacial crystallization of a GaBSi2 glass with Al-441SS substrate after 500h at 850 C



Crystals are $KSrSiO_6$

GaSiB Glasses – No qualitative changes in Reactivity and Stability in Dry 4% Hydrogen

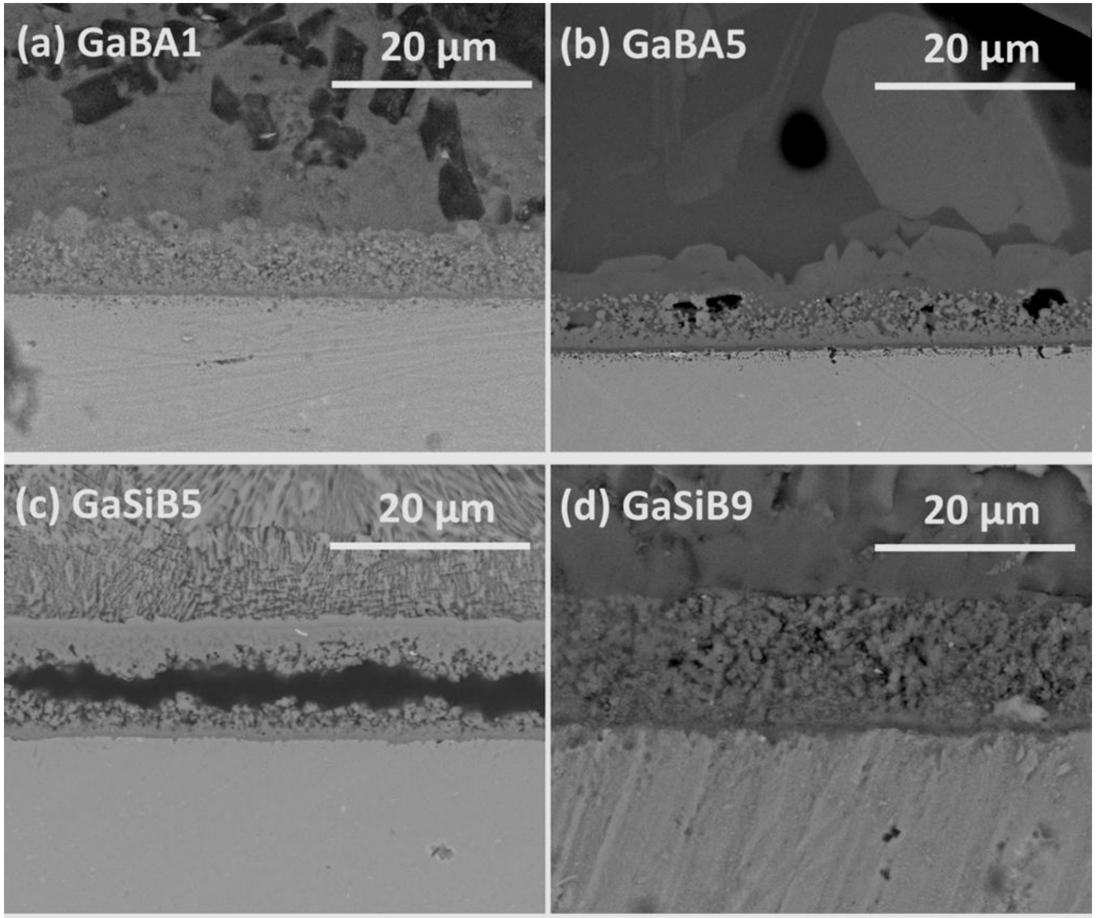
Interfaces bonding with alumina coated 441 stainless steel
Thermal treated after 100 hrs at 750 C



Glasses Chemically Compatible with Spinel Coating

All samples tested with spinel coated SS fail in the spinel coating after 100 h test at OT

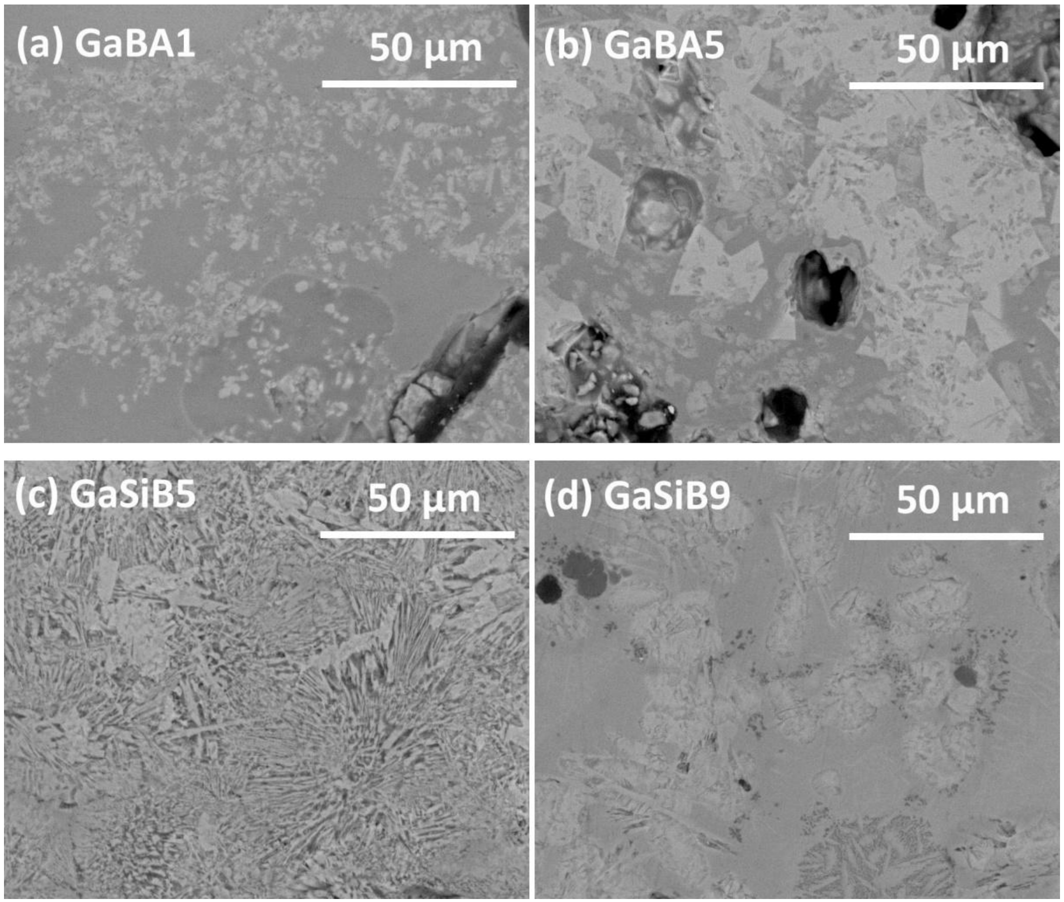
Spinel coating



Spinel coating

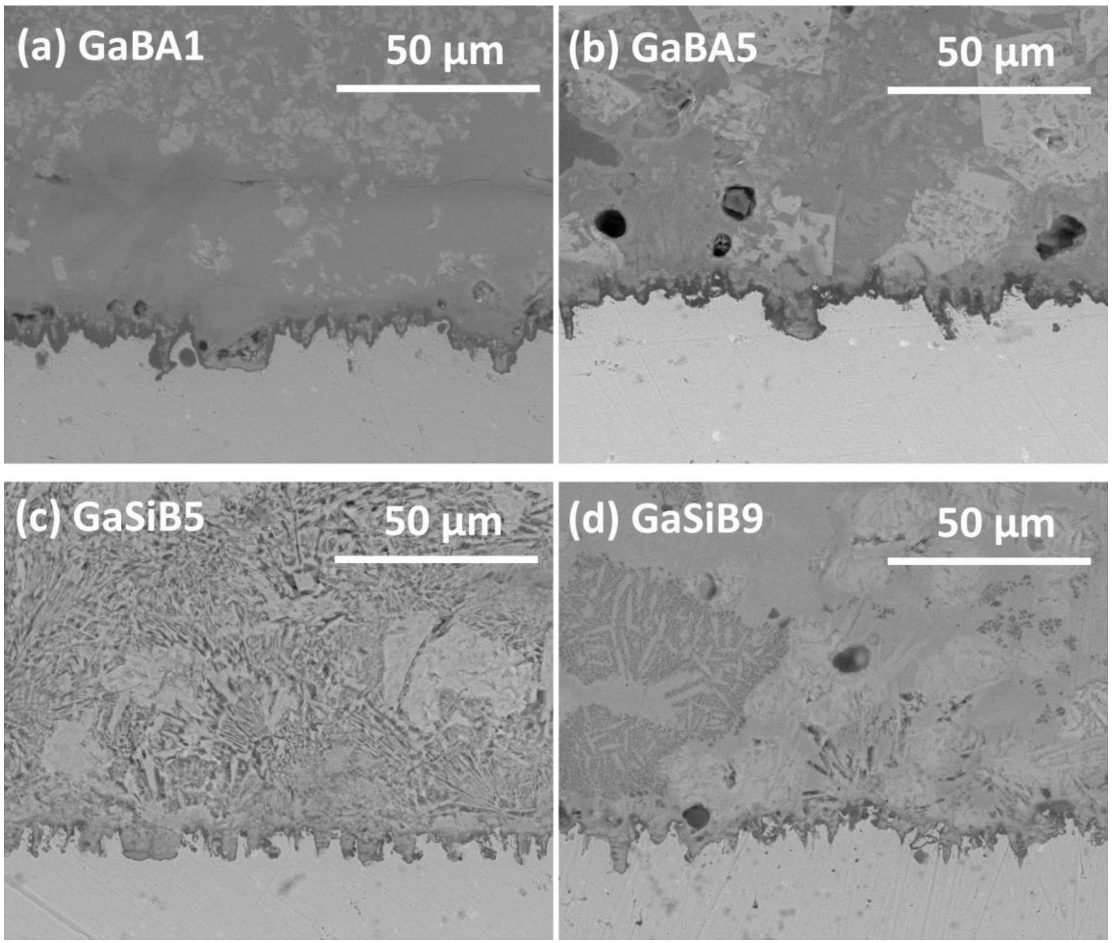
GaBa & GaSiB Stability over 500h in Air

500h at 850 C (GaBA glasses) and 750 C (GaSiB glasses)



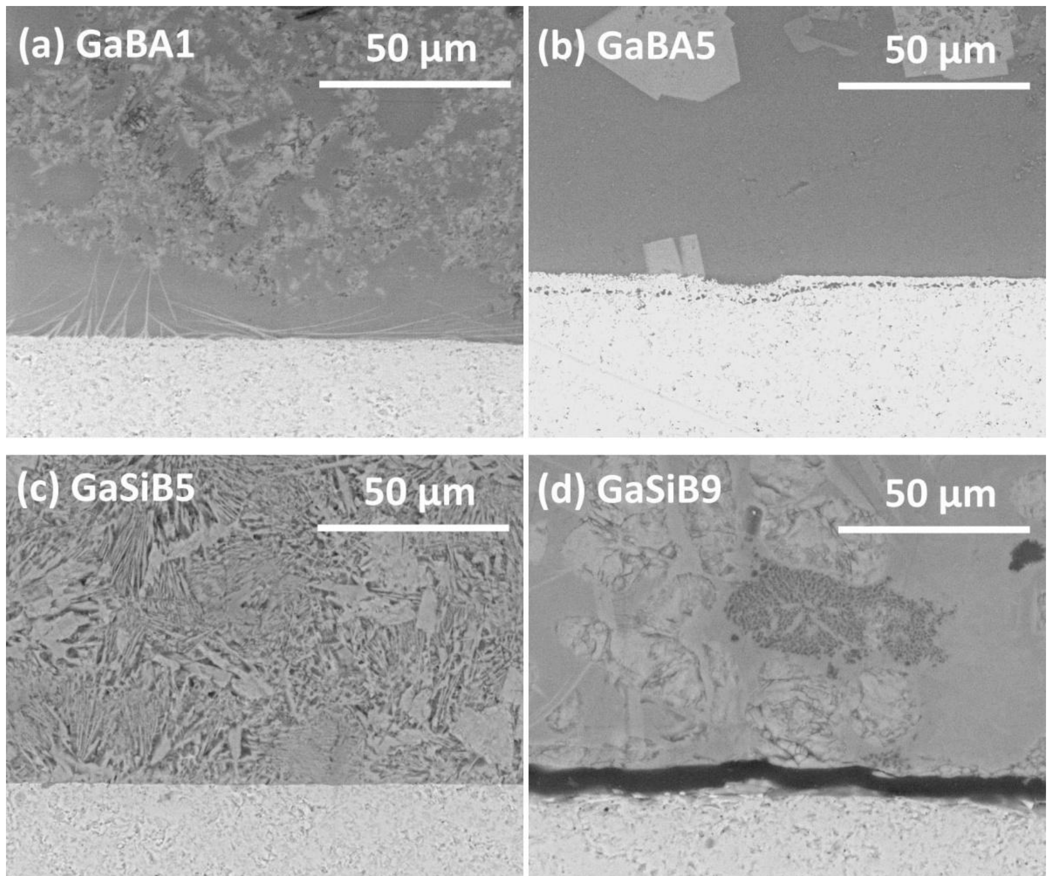
No Effect of Alumina Coating over 500h in Air

Compatibility with protective Al_2O_3 coatings: 850 C (GaBA glasses) and 750 C (GaSiB glasses)



Again 8YSZ inhibits interfacial crystallization and zirconates from at the YSZ interface by 500h

Reactivity with 8YSZ: 500h 850 C (GaBA glasses) and 750 C (GaSiB glasses)

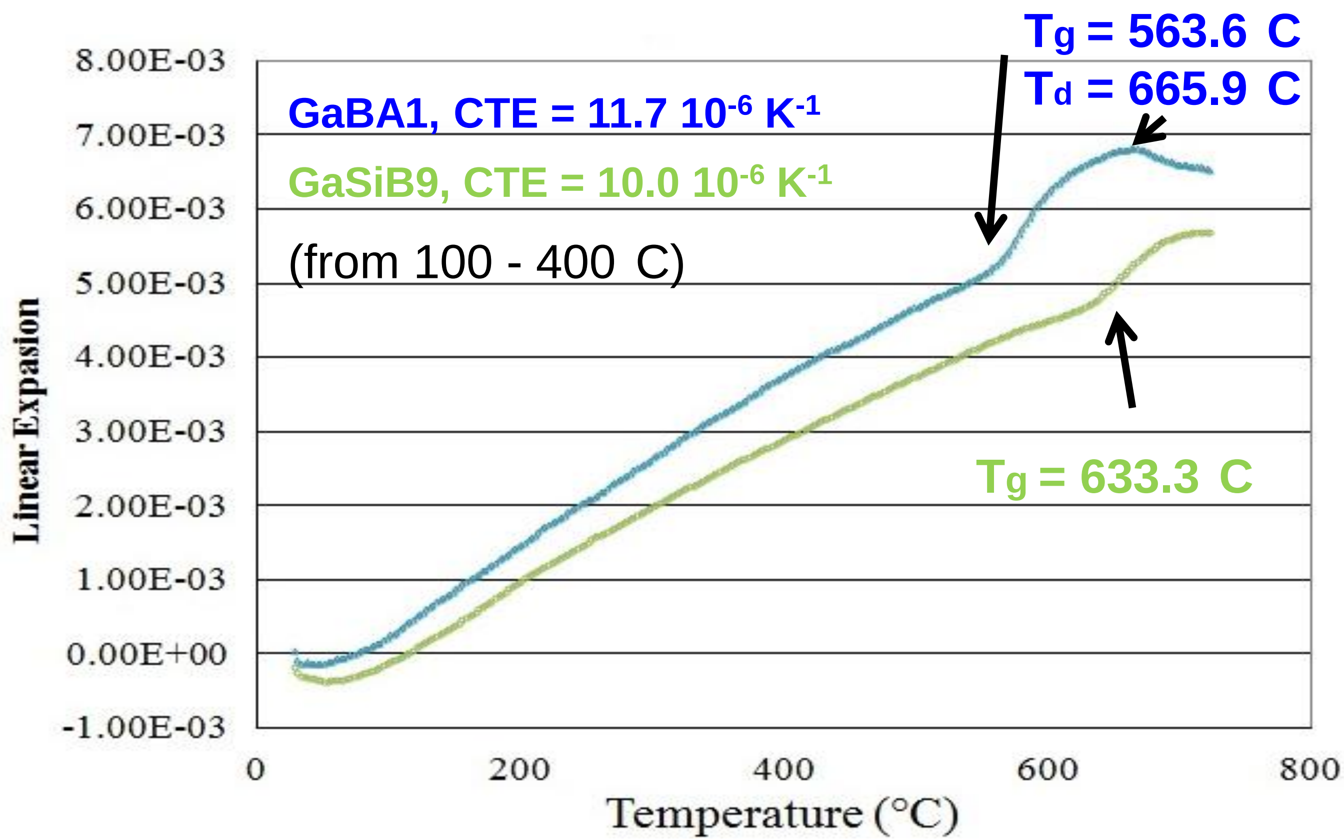


Weight loss of Glasses after 500 h of thermal treatment

Weight loss after 500 hrs at each temperature
Weight loss all less than 1%, alkali-free glasses (GaSiB) even less

	Glass	Treatment	Weight Loss (%)
Low Alkali	GaBA1	850 C, 500h	0.69
	GaBA5	850 C, 500h	0.87
Alkali-free	GaSiB5	750 C, 500h	0.03
	GaSiB9	750 C, 500h	0.16

Thermal Expansion Behavior – Significant Glass Fraction after 500 h with high CTE



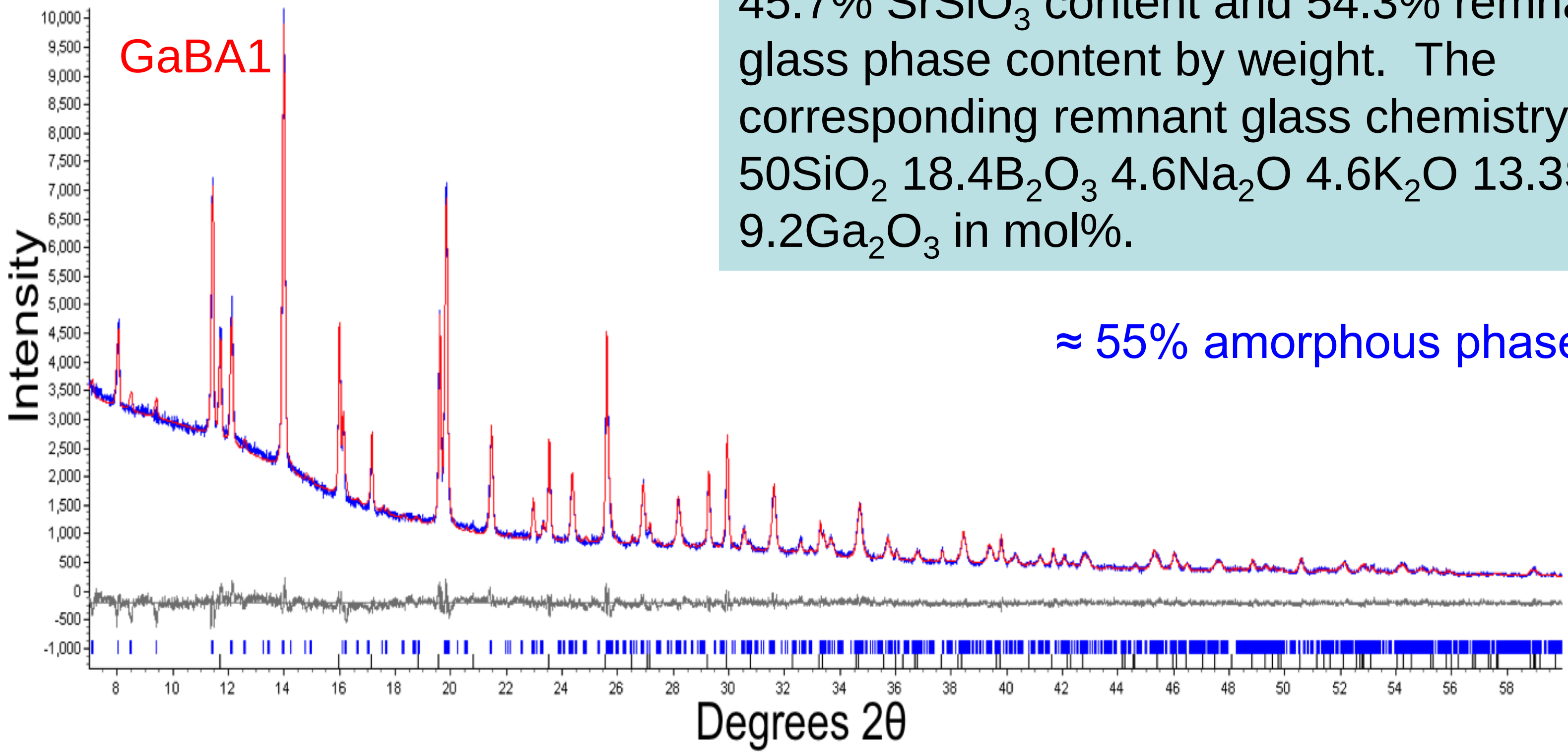
Before thermal treatment (from 100 - 400 C)

GaBA1, CTE = 9.7 10^{-6} K^{-1}

GaSiB9, CTE = 8.3 10^{-6} K^{-1}

Viscous Remnant Glass – Made in Pure Form

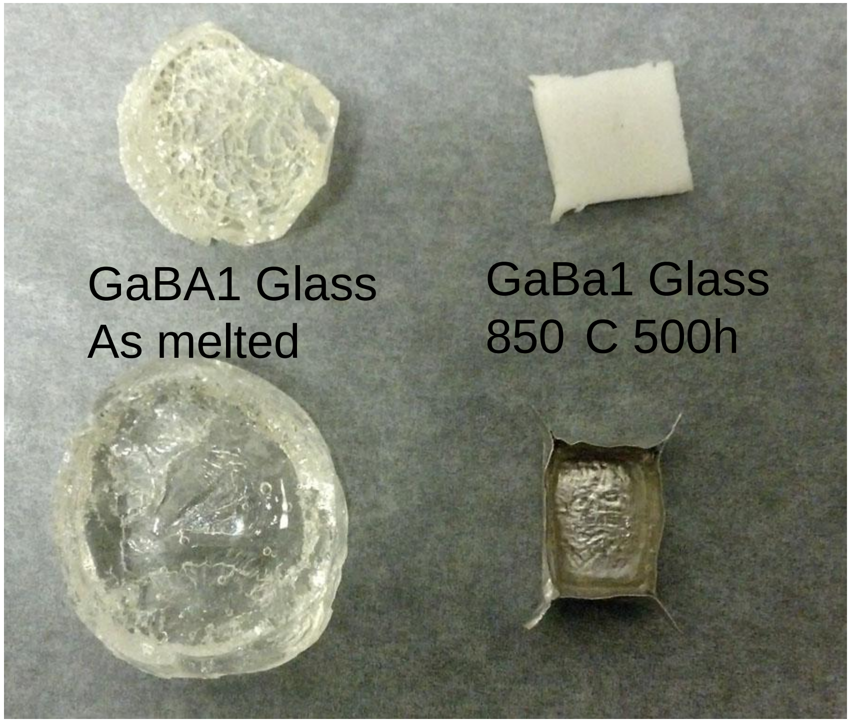
Rietveld analysis allowed calculation of 45.7% $SrSiO_3$ content and 54.3% remnant glass phase content by weight. The corresponding remnant glass chemistry is $50SiO_2$ $18.4B_2O_3$ $4.6Na_2O$ $4.6K_2O$ $13.3SrO$ $9.2Ga_2O_3$ in mol%.



≈ 55% amorphous phase

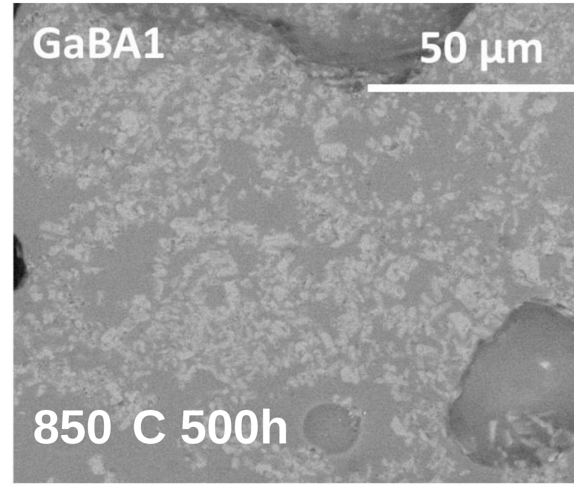
Remnant Glass Does NOT Crystallize Easily

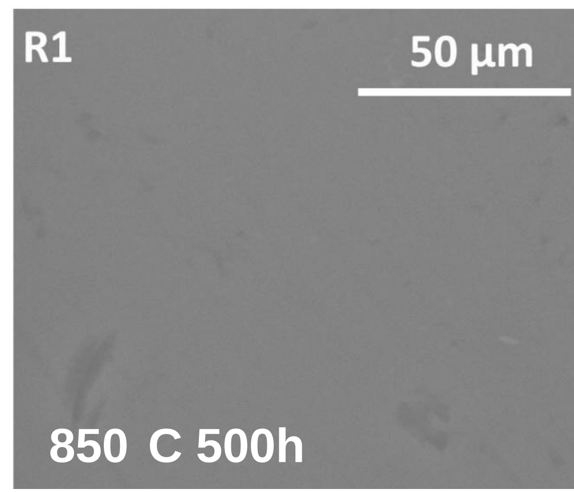
850 C 500h: GaBA1 and R1 (the remnant glass based on GaBA1)



R1 Glass
As melted

R1 Glass
850 C 500h

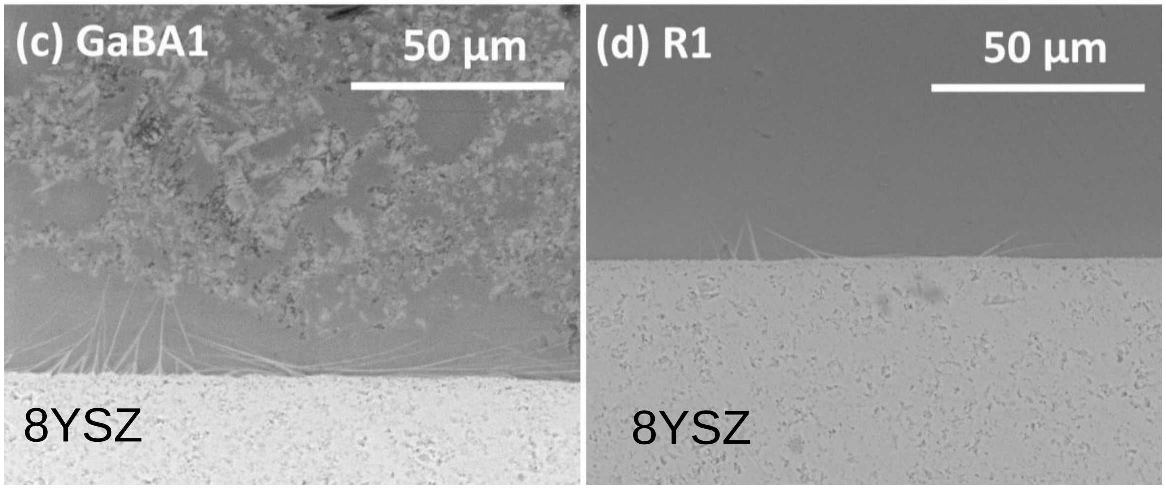




R1 glass lost 2.8% of weight after 850 C 500h, due to its high alkali and boron contents

Interface with YSZ same as for parent glass

850 C 500h: GaBA1 and R1 (the remnant glass based on GaBA1)

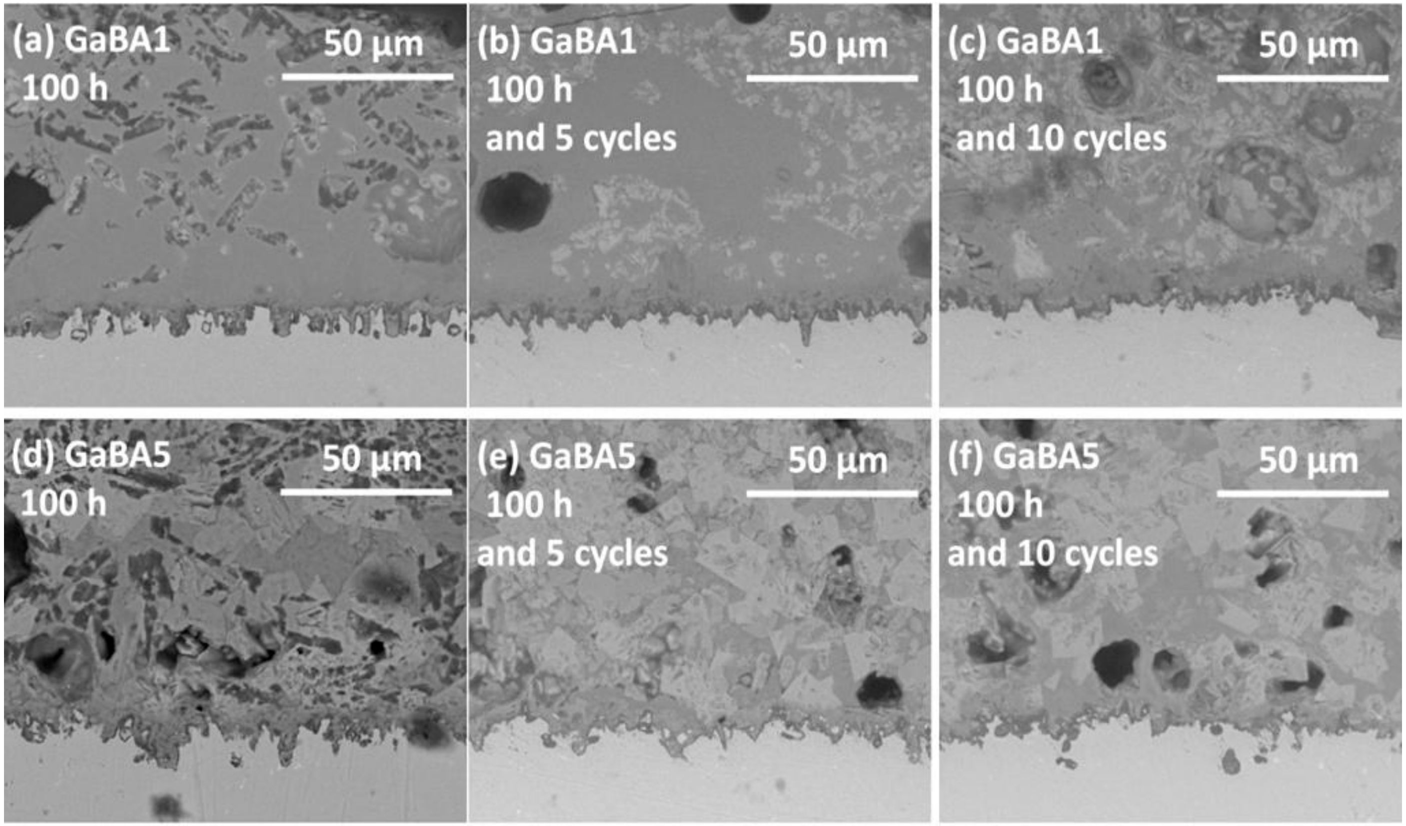


Very similar Sr zirconate crystals at the interface with 8YSZ

NO bulk crystallization

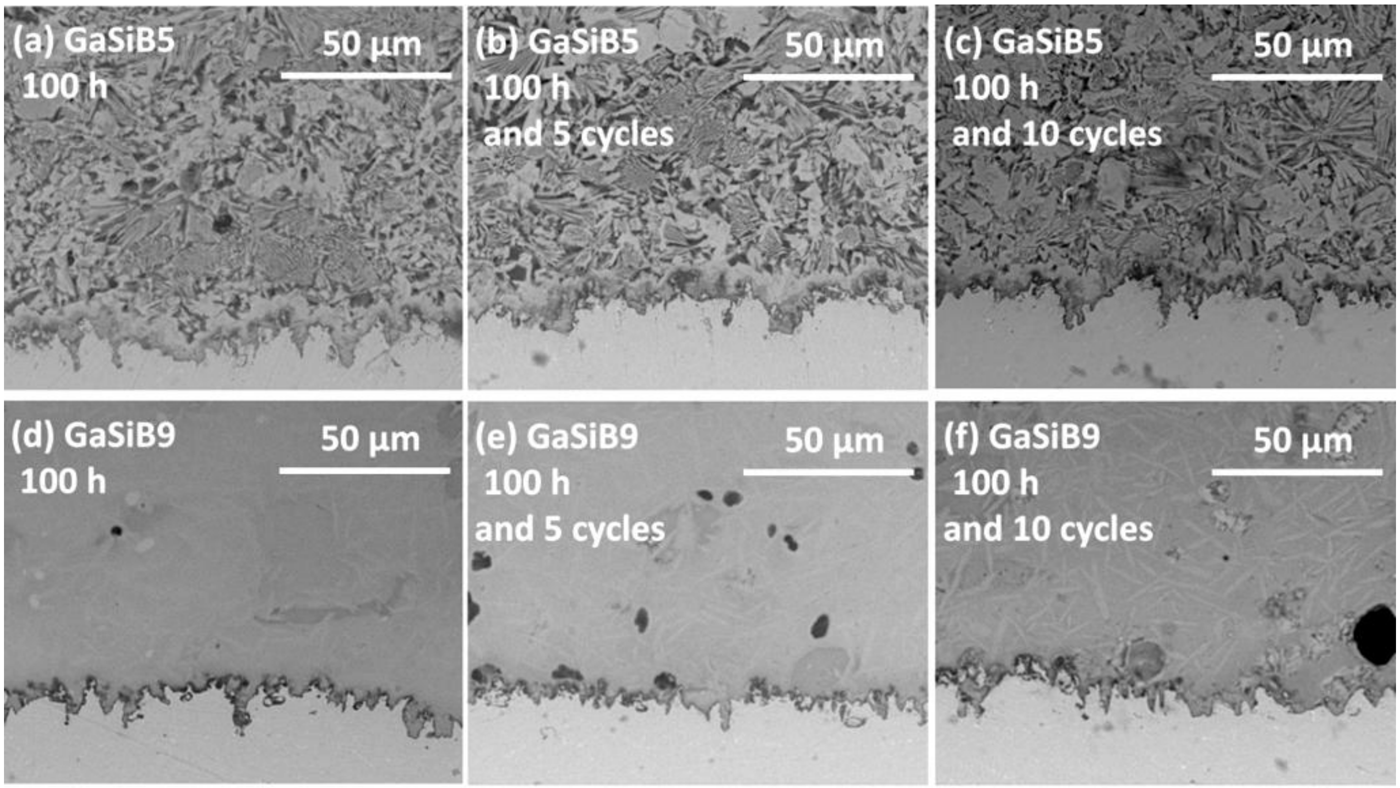
Some GaBA glasses may crystallize further during thermal cycles

After 100 h thermal treatment at OT, samples were cycled using heating and cooling rates of 5 K/min.



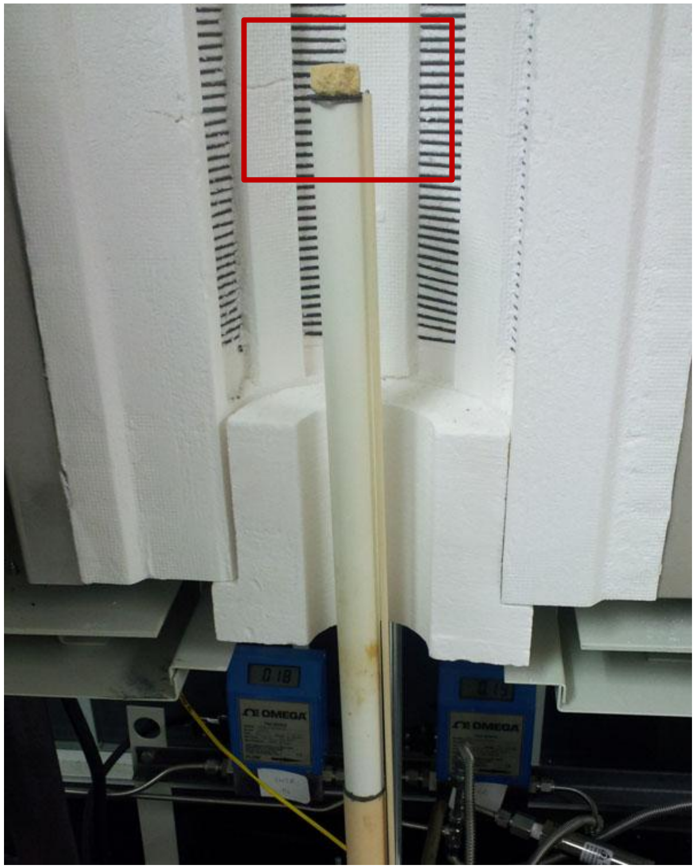
GaSiB Glasses – No Changes During Thermal Cycling

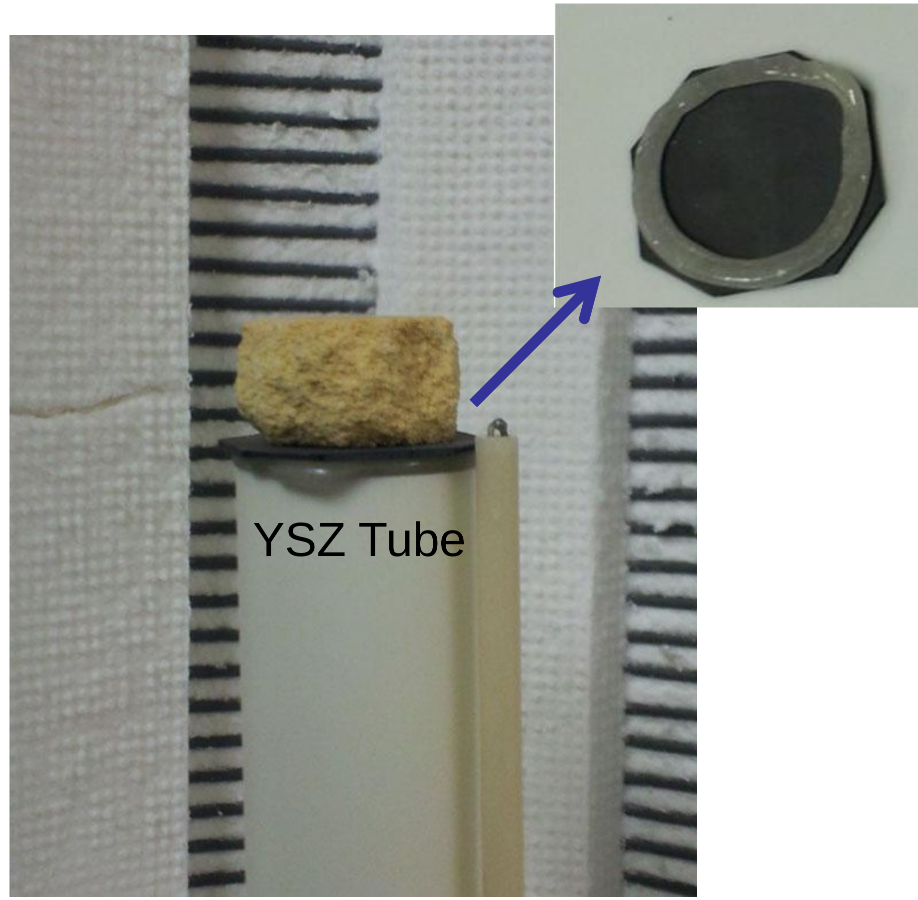
GaSiB5 with extensive crystal phase are stable during thermal cycles
GaSiB9 shows increasing crystals



Sealing Test in SOFC Single Cell Test System

Al-coated SS sealed to YSZ tube

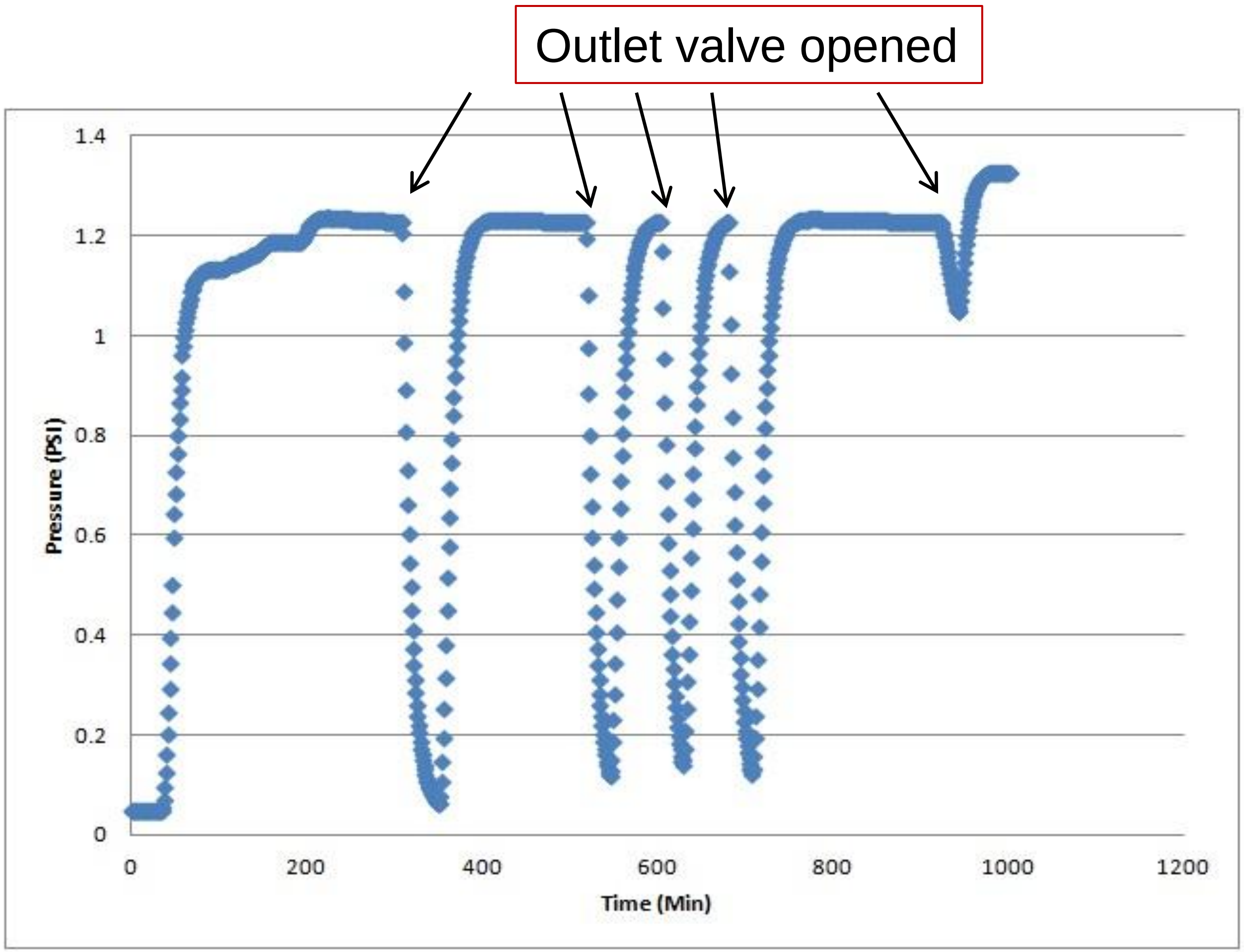




Sealing Test with Thermal Cycling

- GaBA1 sealed with 8YSZ at 850 C: Can be cycled RT to OT without cracking
- Accommodate working pressures of 1.2 psi

GaBA1



Current-Year Summary

- Downselected glasses perform well under dry H_2 and with temperature cycling to 10 cycles.
- New viscous glass compositions based on remnant glass phase show no bulk crystallization but higher weight loss.

Ongoing Work

- Testing glasses under wet 100% H_2
- Additional chemical mapping
- Additional properties measurements of remnant glass compositions

Acknowledgments

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