Physical and Microstructural Characterization of Barium Alkali Silicate Glasses

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Outline

• Background
• Experimental Procedure
• Results
• Ongoing and Future Work
Requirements for SOFC seals

• Simultaneous fulfillment of thermal, physical, chemical, mechanical and electrical property requirements.

• Phase stability and chemical compatibility without substantial property degradation for 40,000 hours in oxidizing and wet reducing environments.

Objective

• To characterize the microstructural evolution of candidate glasses for SOFC sealing applications when exposed to SOFC relevant environments.

• To develop models to predict microstructural changes for periods of time relevant to SOFC sealing applications.
Barium alkali silicate glasses

Two commercially available barium alkali silicate glasses are being investigated

• SCN (SEM-COM Co. Inc., Toledo, OH 43623)
• G6 (Whatman, Piscataway, NJ 08855)

Mechanical and Thermophysical Properties

• Elastic constants
• Thermal expansion
• Glass transition temperature
• Viscosity
• Chemical Composition

• Phase Analysis
• Wetting Behavior (alumina, zirconia)
• Microstructure
• Porosity and its evolution
• Rates of crystallization
Experimental

cold compressed
glass powders

Al$_2$O$_3$ or 8YSZ substrates

after sintering in air
for 2 hours at 850°C
Experimental (cont.)

- Test specimens are exposed to **air** or a gas mixture of \( \text{H}_2 + \text{N}_2 + \text{H}_2\text{O} \) at **850°C**.
- Test specimens are retrieved from the furnace every 1,000 hrs for non-destructive examination (SEM, XRD).
Experimental (cont.)

- Scanning electron microscopy
- EDS
- X-ray diffraction
Experimental (cont.)

• Test specimens are exposed to air or a gas mixture of $H_2+N_2+H_2O$ at 850°C.

• Test specimens are retrieved from the furnace every 1,000 hrs for non-destructive examination (SEM, XRD). Then they are returned to continue exposure.

• After predetermined periods of time, test specimens are removed for destructive examination (SEM, XRD, Tg, viscosity)
Experimental (cont.)
Experimental (cont.)

• Scanning electron microscopy
• EDS

X-ray diffraction
Experimental (cont.)

• To date we have completed the analysis of test specimens of SCN and G6 exposed for 10,000 hrs in air and $\text{H}_2+\text{N}_2+\text{H}_2\text{O}$

• Two sets of test specimens continue exposure tests (12,000+ hrs)
Results
Thermal Expansion and Glass Transition Temperature

Thermomechanical Analyzer

- Al$_2$O$_3$ disk
- Pt foil
- Test specimen

Graph showing dimensional change vs. temperature for G6.
Thermal Expansion

G6

8.0 \times 10^{-6} \, ^\circ C^{-1} \ (100^\circ C) \\
10.6 \times 10^{-6} \, ^\circ C^{-1} \ (450^\circ C)

SCN

10.3 \times 10^{-6} \, ^\circ C^{-1} \ (100^\circ C) \\
12.4 \times 10^{-6} \, ^\circ C^{-1} \ (400^\circ C)
Glass Transition Temperature

![Graph showing dimensional change vs. temperature for G6 material. The graph indicates a sharp transition at around 600°C, which is a typical characteristic of the glass transition temperature.](image-url)
Glass Transition Temperature

![Graph showing the Glass Transition Temperature over time for different conditions.](image)

- **SCNP-Air**: Open circles
- **SCNP-H₂+N₂+H₂O**: Filled circles
- **G6-Air**: Open triangles
- **G6-H₂+N₂+H₂O**: Filled triangles

Legend:
- Force: 0.1N

**Axes**:
- Y-axis: Tg (°C)
- X-axis: Time (hrs)
- X-axis values: As-Sintered, 500, 850, 5,000, 10,000

**Graph Analysis**:
- The plot compares the glass transition temperature (Tg) for different samples under varying conditions over time.
- Each condition has a distinct marker, helping to distinguish between them.
- The graph shows how Tg changes with time for each condition.
Viscosity of G6 Glass

Viscosity Measurements with TMA

- Isothermal conditions (different temperatures between 600°C and 850°C) at 3 different loads (according to ASTM standard C1351)
- Constant heating rate (1°C/min) under a constant load (0.25N)
Viscosity of G6 Glass

Heating Rate: 1°C/min
Force: 0.25N
Chemical Analysis

• Performed a study to assess the precision of different chemical analysis methods \((\text{Al, B, Ba, Ca, Fe, K, Li, Mg, Na, Si, Ti, Zn, Zr})\)
  • Neutron Activation Analysis
  • Inductively Couples Plasma Atomic Emission (ICPAES)
  • Inductively Couples Plasma Mass Spectroscopy (ICPMS)

• Sample Preparation Requirements
• ICPAES is the most precise of the three methods (except for Fe and Zr)
Chemical Analysis using Atom Probe
Select ROI and use FIB to lift out 3 x 25 um² wedge

Cover ROI with protective Pt deposition (IB deposition at 30kV)

Mill trenches around ROI

ROI lift-out with probe needle
Mount slices on microtip and sharpen for APT

Attach to micropost

30kV 280 pA ion beam annular pattern

Trim square

30kV 28pA ion beam annular pattern

Sharpen w. annular milling pattern

Touch up with 5kV 15pA ion beam
3D LEAP reconstruction

3,997,448 ranged atoms in 70 x 70 x 109 nm³
Reconstructed Volume
LEAP mass spectrum

3,997,448 ranged atoms in 70 x 70 x 109 nm³ box
## Composition SCN Glass

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<tr>
<th></th>
<th>ICPMS (ORNL)</th>
<th>ICPAES (ORNL)</th>
<th>APT Tip 1 R06_15869</th>
<th>APT Tip 2 R06_15853</th>
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<td></td>
<td>at.%</td>
<td>at.%</td>
<td>at.%</td>
<td>statistical error (at.%)</td>
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<td>66.67</td>
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<tr>
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<td>Ti</td>
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<td>Li</td>
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<td>H**</td>
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<td>100</td>
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ND = not detected

* Oxygen normalized to SiO$_2$ stoichiometry for ICPMS and ICPAES

** Hydrogen from OH and OH$_2$ molecular ion peaks
Elastic Constants

Elastic Constants

Using results from chemical analyses, an elastic modulus of 70 GPa is predicted at room temperature for SCN glass.

Accounting for 18% porosity, the resulting elastic modulus is 57.4 GPa, which is consistent with values determined by resonant ultrasound spectroscopy.

\[ E = 2V_t \sum G_i X_i, \]

The packing density \( V_t \) is defined by,

\[ V_t = \frac{\rho}{M} \sum V_i X_i, \]

- \( G_i \): Dissociation Energy,
- \( V_i \): Packing factor.
Elastic Constants

Resonant Ultrasound Spectroscopy

Graph showing the change in Elastic Modulus (GPa) with Temperature (°C) for G6 and SCN materials.
Microstructural Analysis

SCN
Porosity Evolution

G6

SCN

Air  Steam+H₂+N₂

As-sintered

100 hrs

500 hrs

850 hrs

5000 hrs

10,000 hrs

% Porosity

Time (hrs)

SCNP-YSZ-Air
SCNP-YSZ-Steam+H₂+N₂
G6-YSZ-Air
G6-YSZ-Steam+H₂+N₂

OAK RIDGE National Laboratory
Summary of Pores

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<th>Perimeter (um)</th>
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Total Area

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<td>3649080.5</td>
<td>2278.2881</td>
<td>7714.5317</td>
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</table>
Pore Evolution: SCN-YSZ ($H_2+N_2+H_2O$)
Rates of Crystallization

$\text{KAlSi}_3\text{O}_8$

Avrami Exponent = 0.5

$V_f \sim 16\%$

40,000 hours
SCN-YSZ-49

After 10,000 Hours in Steam+$H_2+N_2$
SCN-YSZ-49

After 10,000 Hours in Steam+H₂+N₂
SCN-YSZ-49

After 10,000 Hours in Steam+H₂+N₂
SCN-YSZ-49

After 10,000 Hours in Steam+H$_2$+N$_2$
SCN-YSZ-49

After 10,000 Hours in Steam+H\textsubscript{2}+N\textsubscript{2}
SCN-YSZ-49

After 10,000 Hours in Steam+$H_2+N_2$
SCN-YSZ-49

After 10,000 Hours in Steam+H₂+N₂
SCN-YSZ-49 After 10,000 Hours in Steam+H₂+N₂
SCN-YSZ-49

After 10,000 Hours in Steam+$H_2+N_2$
SCN-YSZ-49

After 10,000 Hours in Steam+H₂+N₂
SCN-YSZ-55

After 10,000 Hours in Air
SCN-YSZ-55

After 10,000 Hours in Air
SCN-YSZ-55

After 10,000 Hours in Air
SCN-YSZ-55

After 10,000 Hours in Air
SCN-YSZ-55

After 10,000 Hours in Air
SCN-YSZ-55

After 10,000 Hours in Air
SCN-YSZ-55

After 10,000 Hours in Air
SCN-YSZ-55

After 10,000 Hours in Air
SCN-YSZ-55

After 10,000 Hours in Air
SCN-YSZ-55

After 10,000 Hours in Air

Elements detected: K, Al, Ca, Na, Ba, O, Si
G6-YSZ-54 After 10,000 Hours in Steam+H$_2$+N$_2$
G6-YSZ-54

After 10,000 Hours in Steam+H₂+N₂
G6-YSZ-54
After 10,000 Hours in Steam+H$_2$+N$_2$
G6-YSZ-54

After 10,000 Hours in Steam+$\text{H}_2+\text{N}_2$
G6-YSZ-54

After 10,000 Hours in Steam+H₂+N₂
G6-YSZ-54

After 10,000 Hours in Steam+H$_2$+N$_2$
G6-YSZ-54

After 10,000 Hours in Steam+H$_2$+N$_2$
G6-YSZ-54

After 10,000 Hours in Steam+$\text{H}_2+\text{N}_2$
G6-YSZ-54

After 10,000 Hours in Steam+H₂+N₂
G6-YSZ-51

After 10,000 Hours in Air
G6-YSZ-51

After 10,000 Hours in Air
G6-YSZ-51

After 10,000 Hours in Air

Elements detected: Na, Si, K, O, Al, Ca, Ba, Mg, Y, Zr.
G6-YSZ-51

After 10,000 Hours in Air
G6-YSZ-51

After 10,000 Hours in Air
G6-YSZ-51

After 10,000 Hours in Air
G6-YSZ-51

After 10,000 Hours in Air
G6-YSZ-51

After 10,000 Hours in Air
G6-YSZ-51

After 10,000 Hours in Air

Elements detected: K, Al, Ca, Mg, Na, Ba, O, Si.
SCN-YSZ (steam): powder XRD

Y0.15Zr0.85O1.93
KAlSi3O8
BaO
Ca₆(SiO₃)₆·6(H₂O)
Ba₅Si₄O₁₂(OH)₂
G6-Al$_2$O$_3$ (Steam): Surface Analysis

5,000 hrs

MgAl$_2$O$_4$

KAISi$_3$O$_8$
SCN-YSZ-73 (air): Surface Analysis

Intensity (arb. units)

2,000 hrs
3,650 hrs
5,000 hrs
6,000 hrs
7,000 hrs
8,000 hrs
9,000 hrs
10,000 hrs
11,000 hrs
12,000 hrs

2-Theta(°)
SCN-Al$_2$O$_3$-64 (steam): Surface Analysis

![XRD graphs showing changes over time](image)

- **2,000 hrs**
- **3,650 hrs**
- **4,000 hrs**
- **5,000 hrs**
- **5,900 hrs**
- **7,030 hrs**
- **9,000 hrs**
- **10,000 hrs**

Chemical compounds identified:
- KAlSi$_3$O$_8$
- BaAl$_2$Si$_3$O$_{10}$
- Corundum, syn-Al$_2$O$_3$
Summary

• The physical and mechanical properties of two barium alkali silicate glasses (SCN, G6) were determined as a function of temperature.
• The microstructure of these glasses has been characterized for up to 10,000 hours in air and $\text{H}_2+N_2+\text{H}_2\text{O}$. Test specimens continue being exposed (12,000+ hrs).
• Models are being developed to predict the rates of crystallization and the evolution of microstructure and physical properties.
• Engineering-based models are being developed to predict the behavior of SOFC seals comprising these glasses.
Dual Environment

- Expose samples at high temperature to both environments: Air and H₂+N₂+Steam simultaneously
- Control flow and pressure of both Environments
- Monitor Output Air Flow to detect sample leaks
Conditions for LEAP analysis

- Tip base temperature 60 K
- Laser wavelength: 355 nm (ultraviolet)
- Laser pulse repetition frequency 250 kHz
- Laser pulse energy 200 pJ (tip 1) or 300 pJ (tip 2)
- Evaporation rate: 0.3-1.0 % ions-per-pulse
- Fraction of “golden” events 68 %

- Two successful runs, one with 2M atoms, the second with 4M atoms in reconstruction
- Both runs terminated by tip fracture
- Reconstruction with $k \times E = 3.3 \times 33 \text{ V/nm}$
- Reconstruction boxes 71 x 71 x 49 nm$^3$ and 70 x 70 x 109 nm$^3$ for the two runs
3D LEAP reconstruction tip 1

2,093,577 ranged atoms in 71 x 71 x 49 nm$^3$
reconstructed Volume
LEAP mass spectrum tip 1

2,093,577 ranged atoms in 71 x 71 x 49 nm³ reconstructed Volume