Thermochemically Stable Sealing Materials for Solid Oxide Fuel Cells

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Designing glasses for SOFC seals is a significant challenge

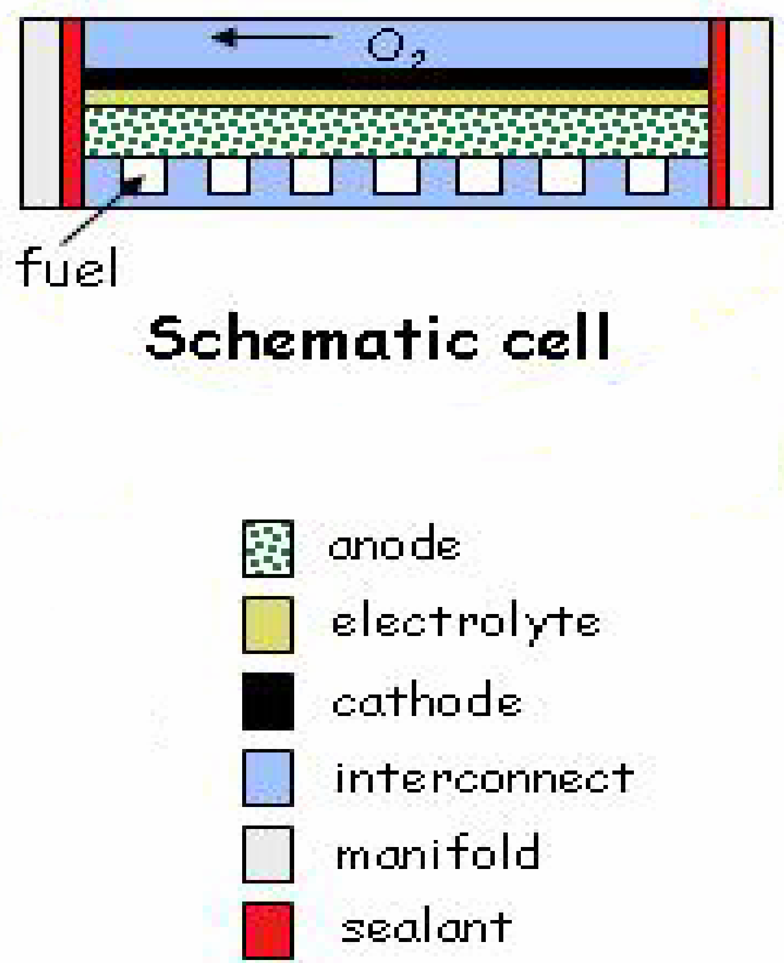
Function:

- Prevent mixing of fuel/oxidant within stack
- Prevent leaking of fuel/oxidant from stack
- Electrically isolate cells in stack
- Provide mechanical bonding of components

Challenges:

- Thermal expansion matches to a variety of materials
- Relatively high operational temperatures (>700°C)
  - Long lifetimes (>10000's hrs)
  - Maintain stability over range of P_{O2}, P_{H2O}
- Relatively low sealing temperatures (<900°C)
  - Avoid altering other SOFC materials

For some designs, glass-ceramics may be suitable



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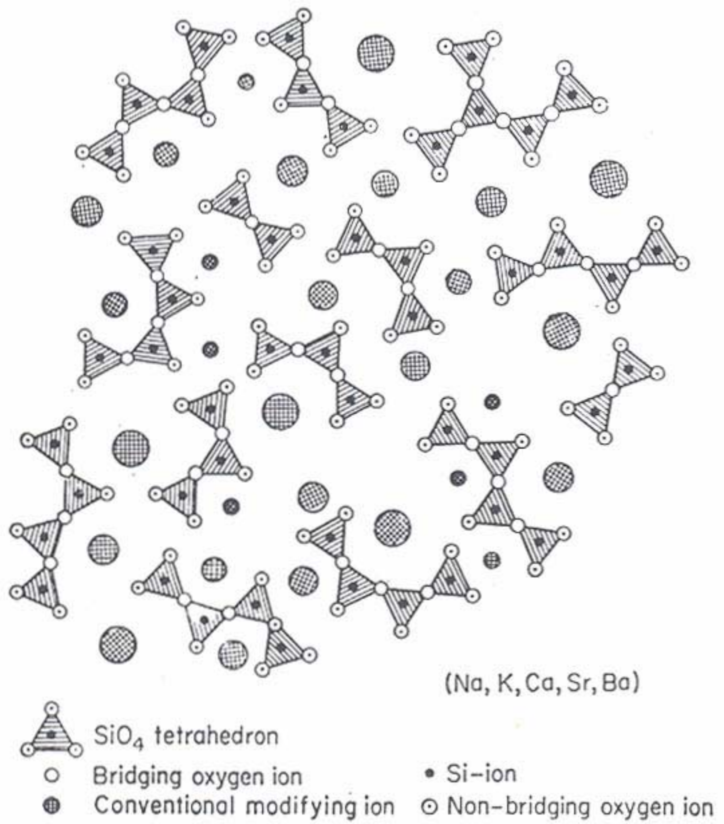
Promising glasses have unusual structures



"**Invert Glasses**": discontinuous silicate anions tied-together through modifying cations.

- Greater CTE's
- More fragile viscosity characteristics
  - 'shorter' glasses
  - More 'basic' reaction chemistries

- Metasilicates (chains): [O]/[Si]~3.0
- Polysilicates (short chains): [O]/[Si]>3.0

UMR glass-ceramics under development

- ZnO-modified alkaline earth invert silicates, mixed CaO, SrO, ZnO (45-55 mole%), BaO-free
  - [O]/[Si]>3.3, SiO_2<45 mole%
  - Minor oxides include Al_2O_3, B_2O_3, TiO_2

Property design targets: Seal/crystallized <850°C
CTE-match to YSZ
Thermomechanically stable at >700°C
Thermochemically stable in oxidizing/reducing conditions

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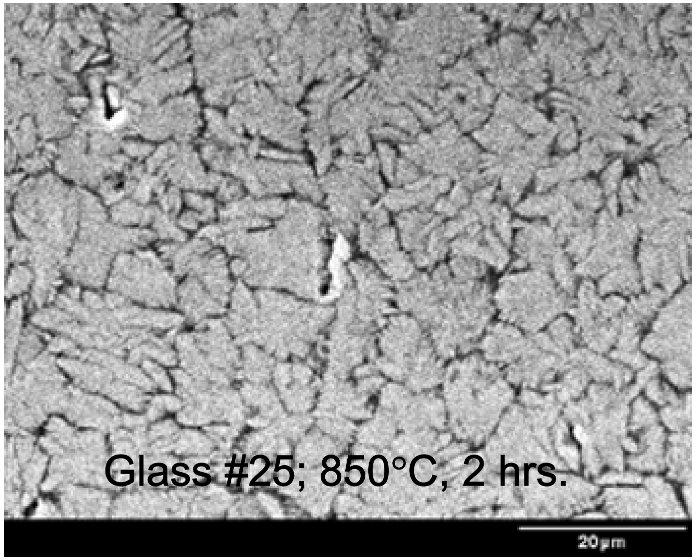
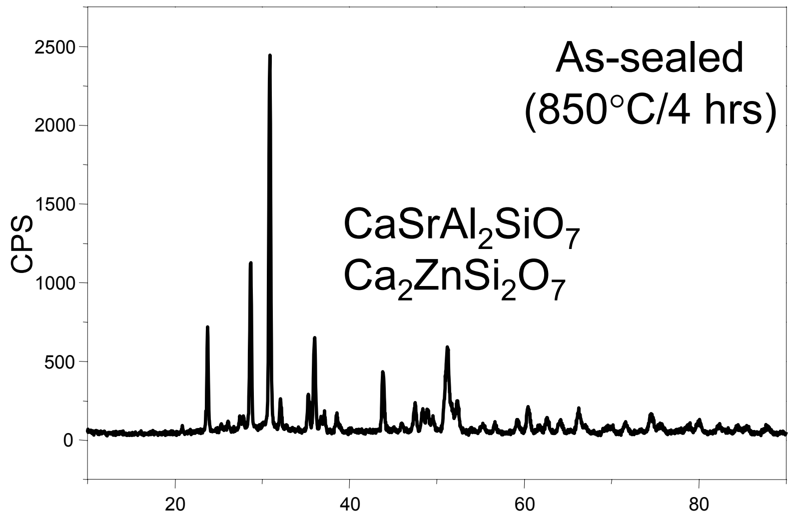
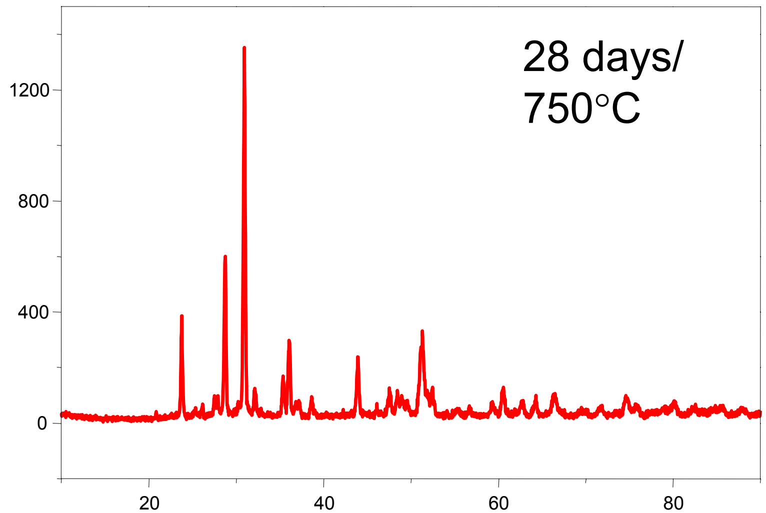
Representative crystalline phases in the UMR glass-ceramics

- **Pyrosilicates**
  - $CaSrAl_2SiO_7$, $Ca_2ZnSi_2O_7$
- **Orthosilicates**
  - Sr_2SiO_4, Zn_2SiO_4
- Composition is most important parameter for final phase distribution.







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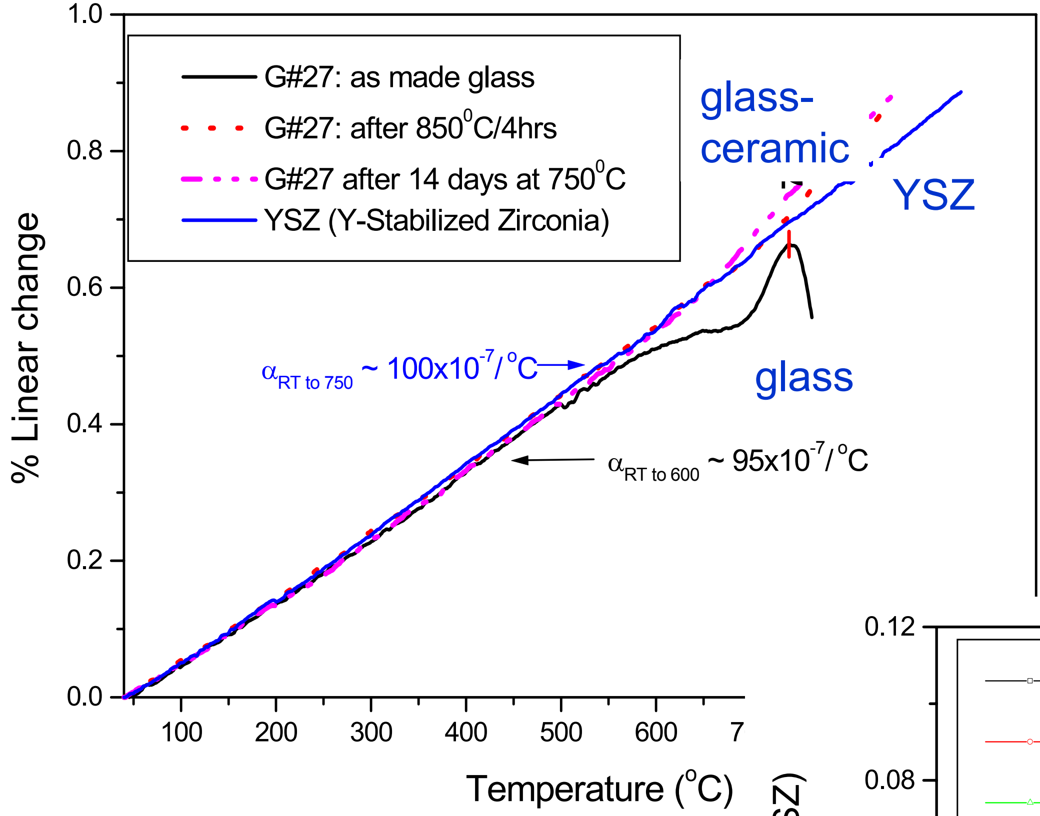
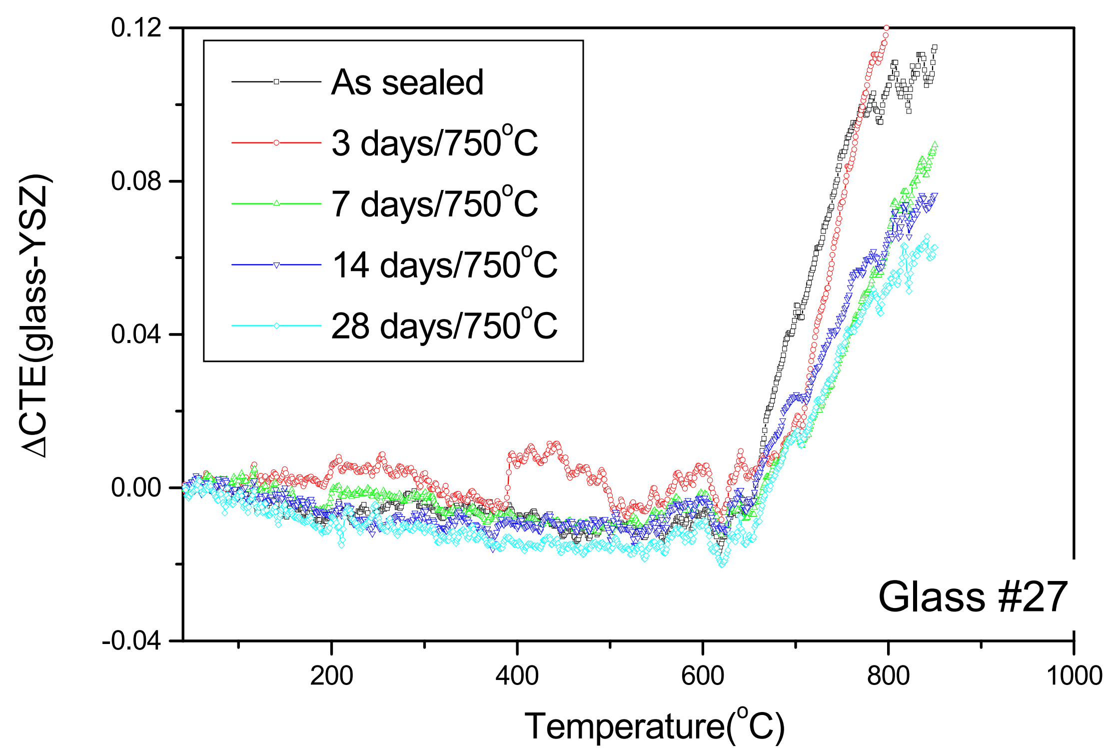
System Glass#27



Dilatometry indicates good CTE-match with YSZ

CTE difference between glass #27 and YSZ- note 'glassy' behavior at T>650°C



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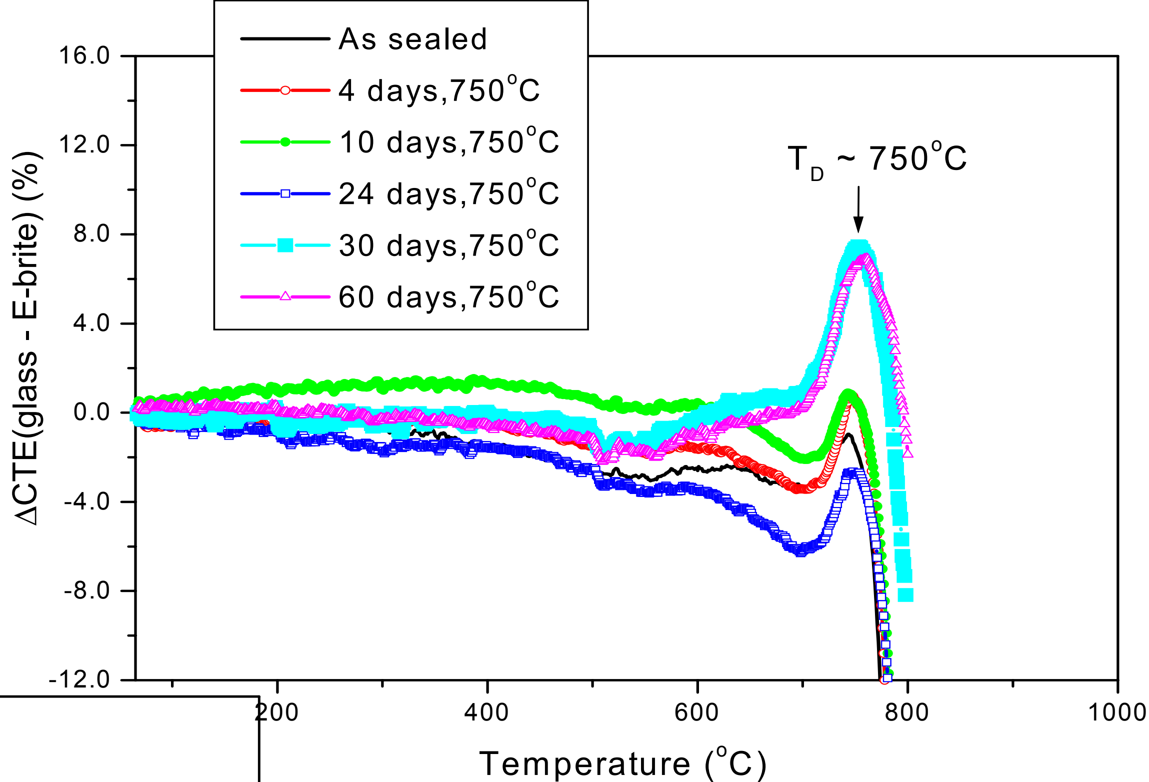
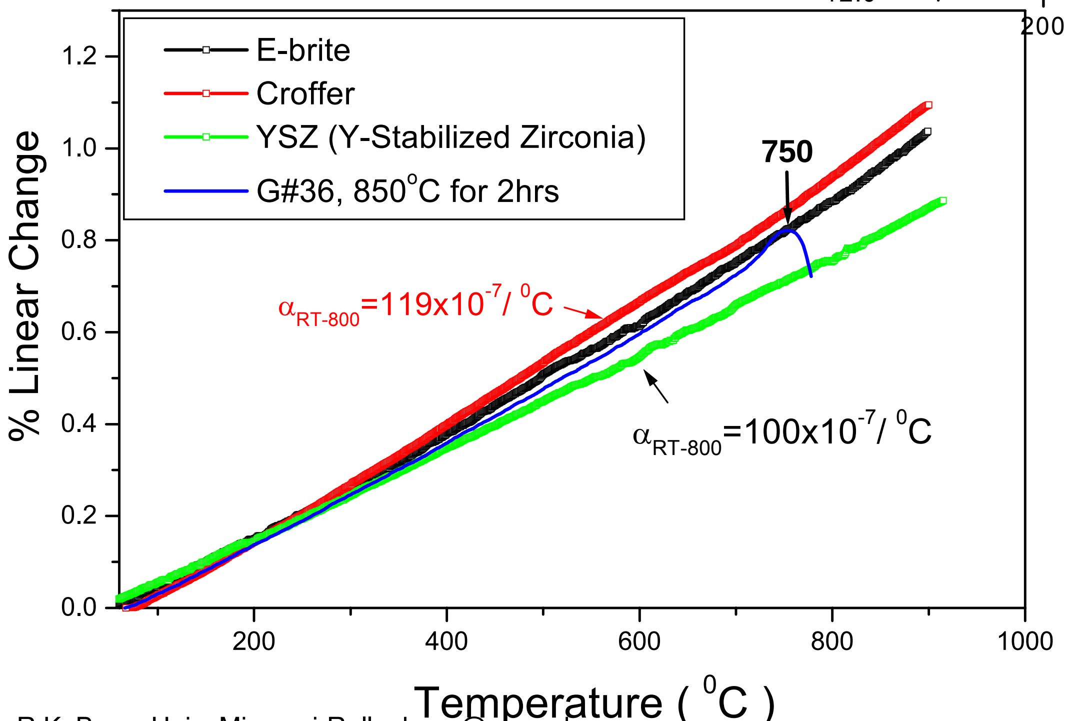
System Glass#36





CTE difference between glass #36 and E-brite - note 'glassy' behavior up 60 days

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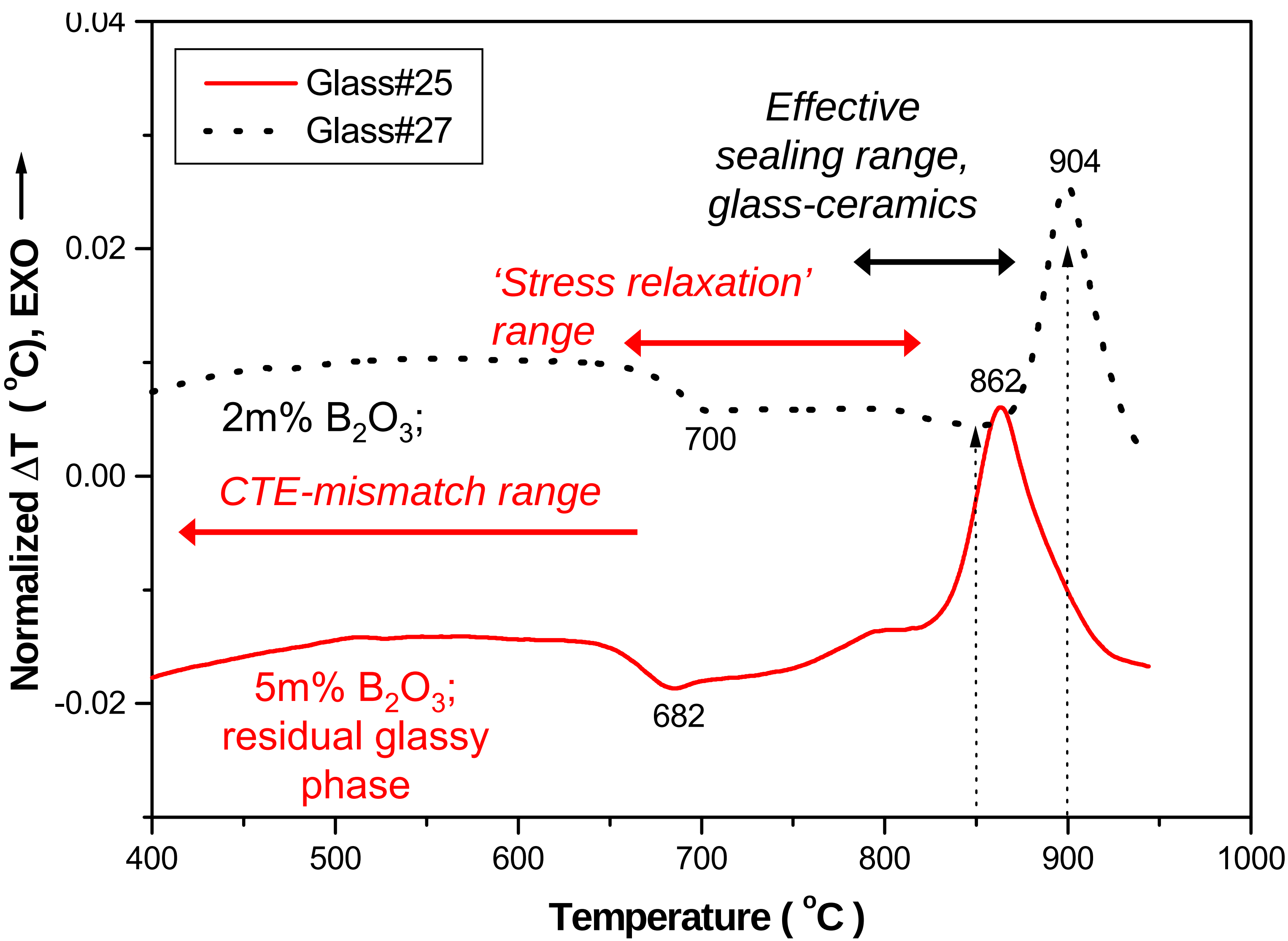
DTA provides information about sealing glasses



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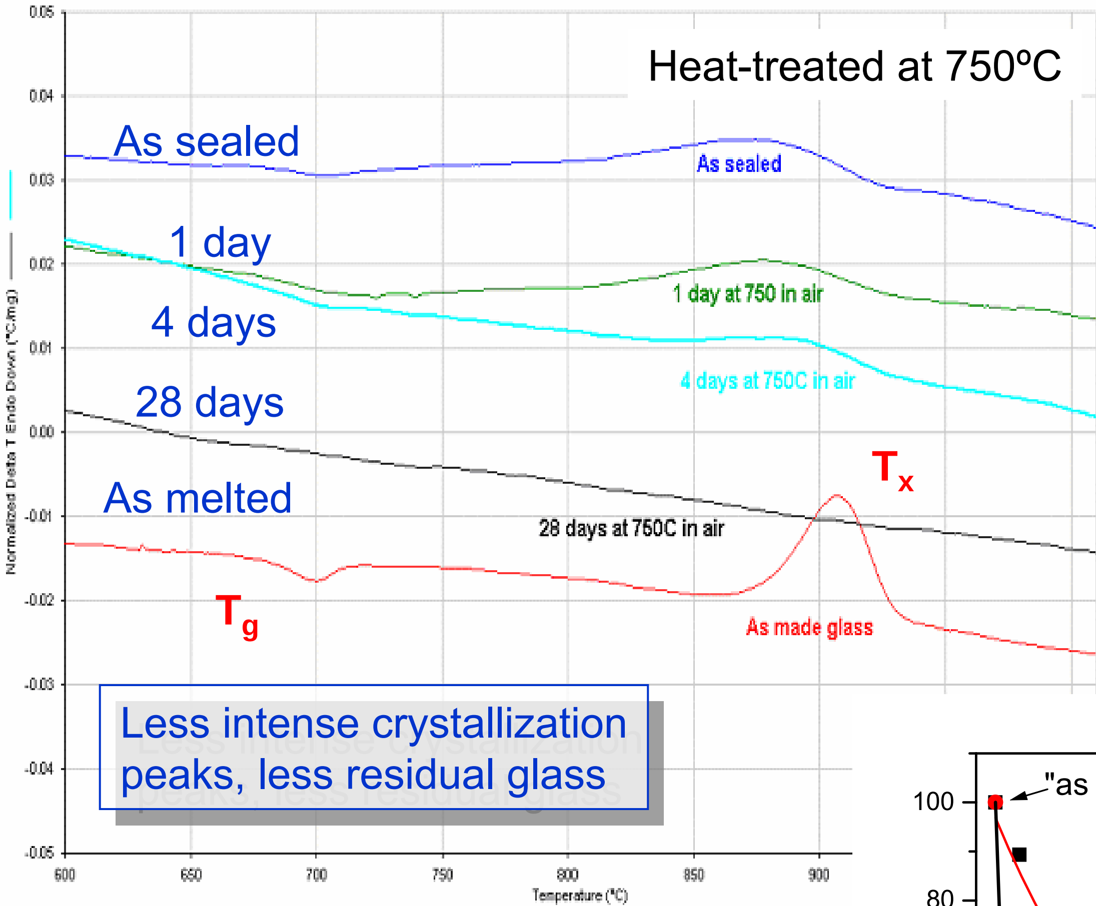
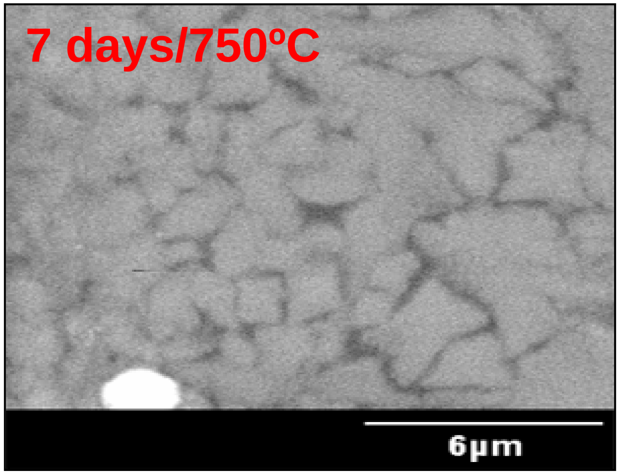
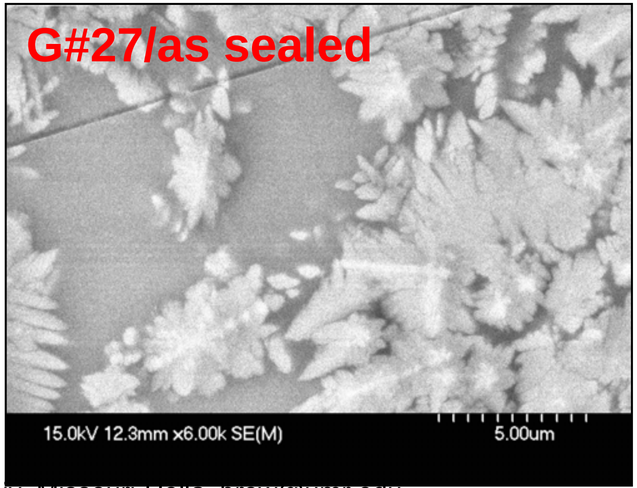
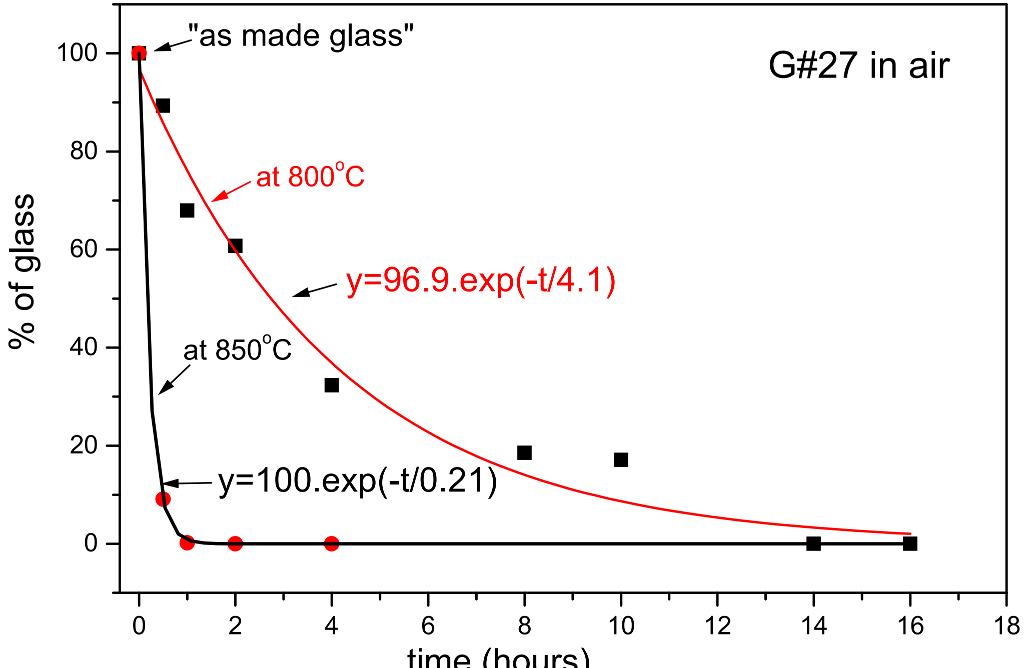
DTA provides information about the nature of the residual glass









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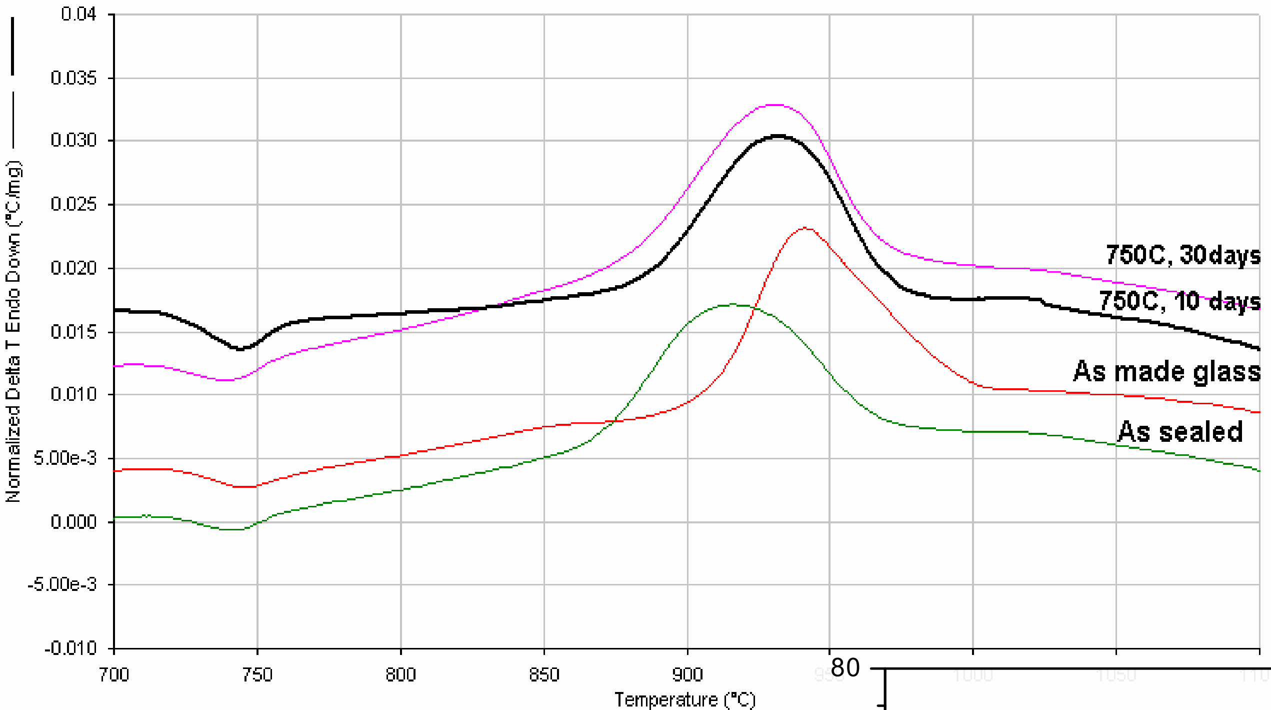
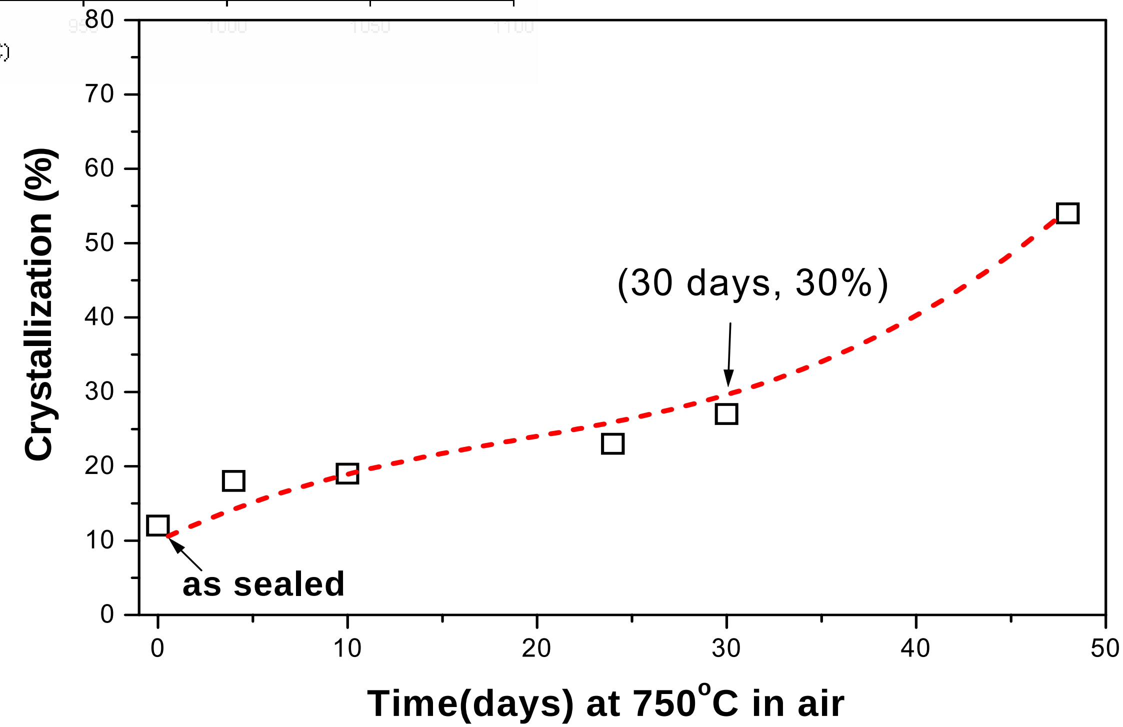


Glass #36 crystallizes more slowly after sealing than G27



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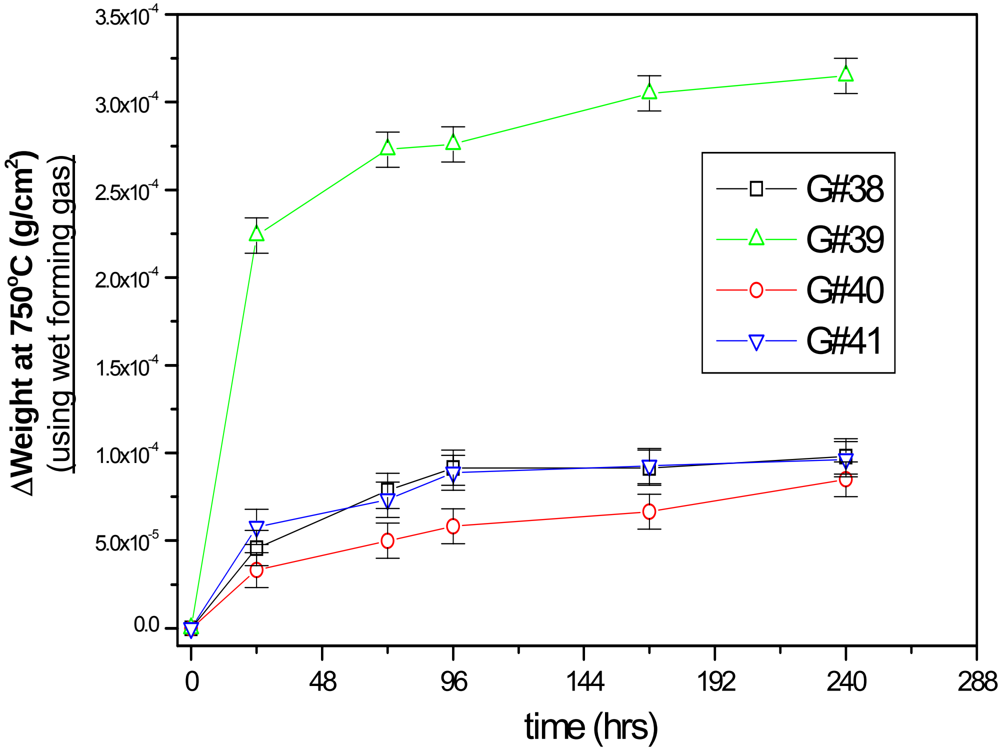
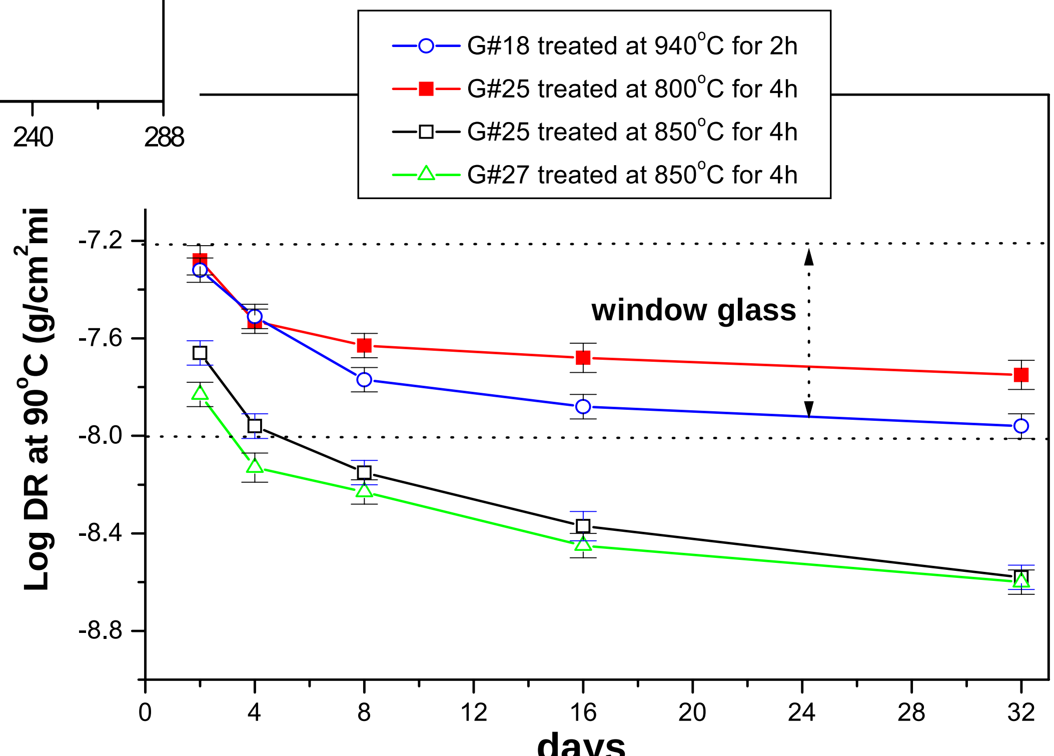
Glass stability in wet forming gas; 750°C



- Higher B_2O_3 contents → less stable
- No correlation between ZnO content and glass stability in reducing environments

Glass stability in water; 90°C



- Glasses are durable (as good or better than window glass
- Crystallized materials are more durable than 'as cast' glass

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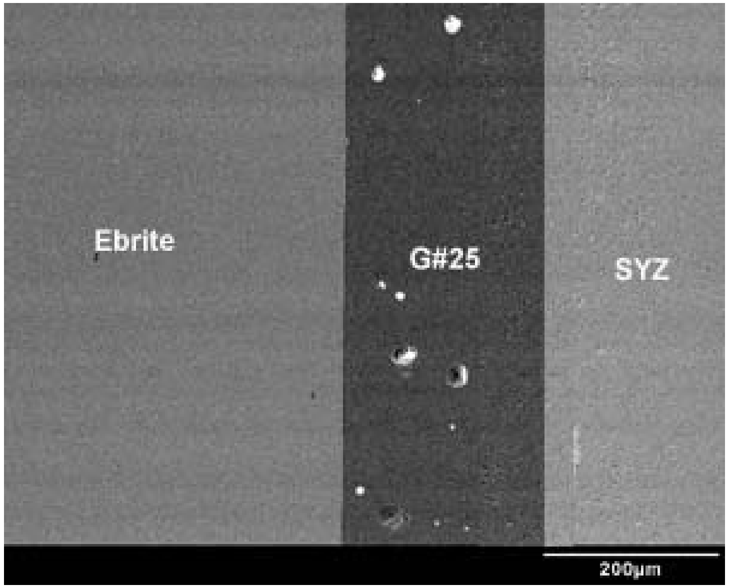
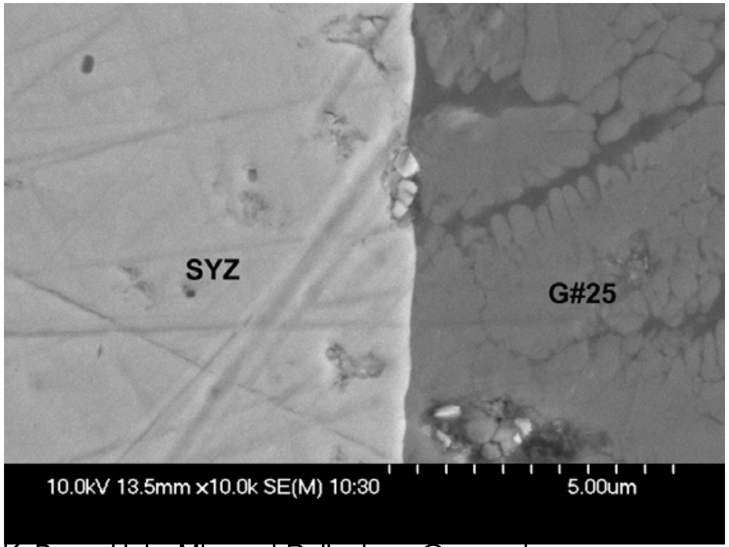
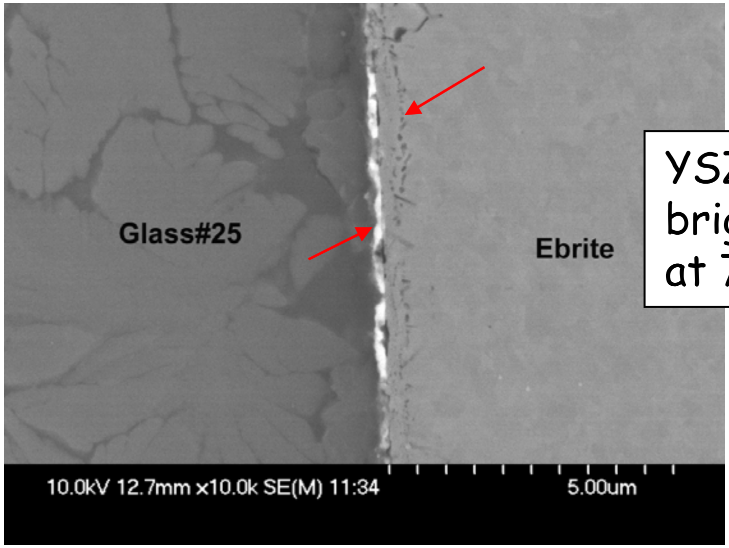
Test seals have been prepared with SOFC coupon materials

- Glass pastes
  - Glass powders, ~45mm & <5mm
  - PVB binders
  - Binder burn out: 500°C/air; glass sealed: 850°C/argon
  - Glass thickness: 20-400mm
- Interconnect alloy: E-bright
  - Cr-ferritic steel (26% Cr)
  - CTE ~ 11.7 ppm/°C
- YSZ coupons (8%Y_2O_3)
  - CTE ~ 10 ppm/°C

"As sealed" Glass 25 paste with YSZ and E-bright substrates (850°C/4hrs, Ar).







YSZ/Glass 25/E-bright after 14 days at 750°C in air.

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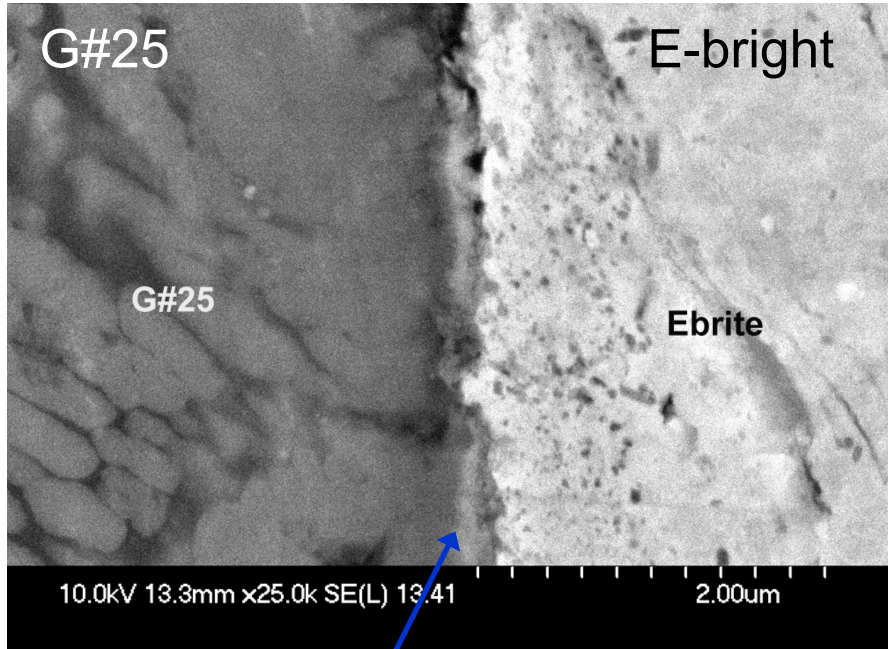
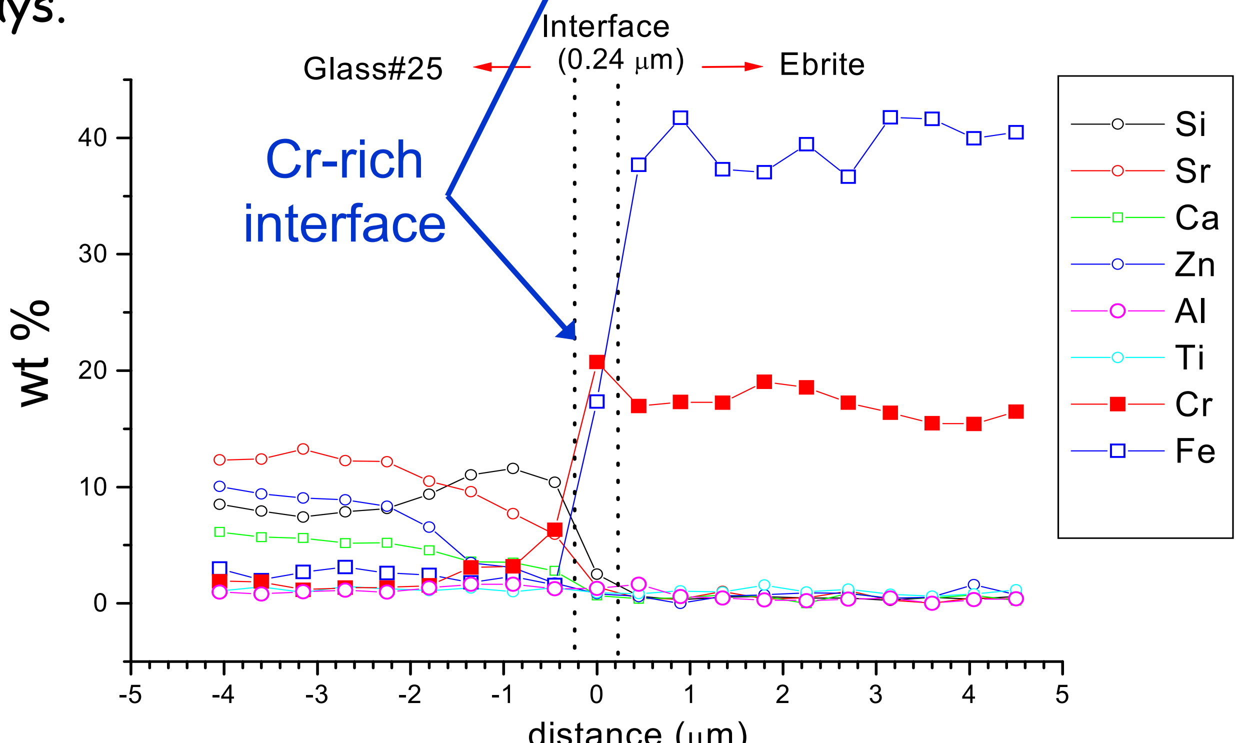
Glass#25/E-brite; 750°C for 14 days.



Cr-rich interfacial reaction products are found at the glass/E-bright interfaces



SOFC Seal Summary

- SOFC seals offer an interesting materials challenge
- 'Invert' polysilicate compositions have promising combinations of properties
  - 'Invert' glass-ceramics can be designed with thermal and chemical properties desired for some SOFC seal designs.
  - Thermo-chemical and thermo-mechanical stabilities are critical for long-term applications.
- Future Work
  - Performance in operating cells and stacks (UMR, UConn)
  - Development of composite sealing materials (UMR, UCincy)
  - Full characterization of glass/metal interfaces (UMR, Sandia)

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