Thermochemically Stable Sealing Materials for Solid Oxide Fuel Cells

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Acknowledgements

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- Dr. Signo Reis and Mr. Teng Zhang (UMR)
- Ron Loehman, Sandia National Labs

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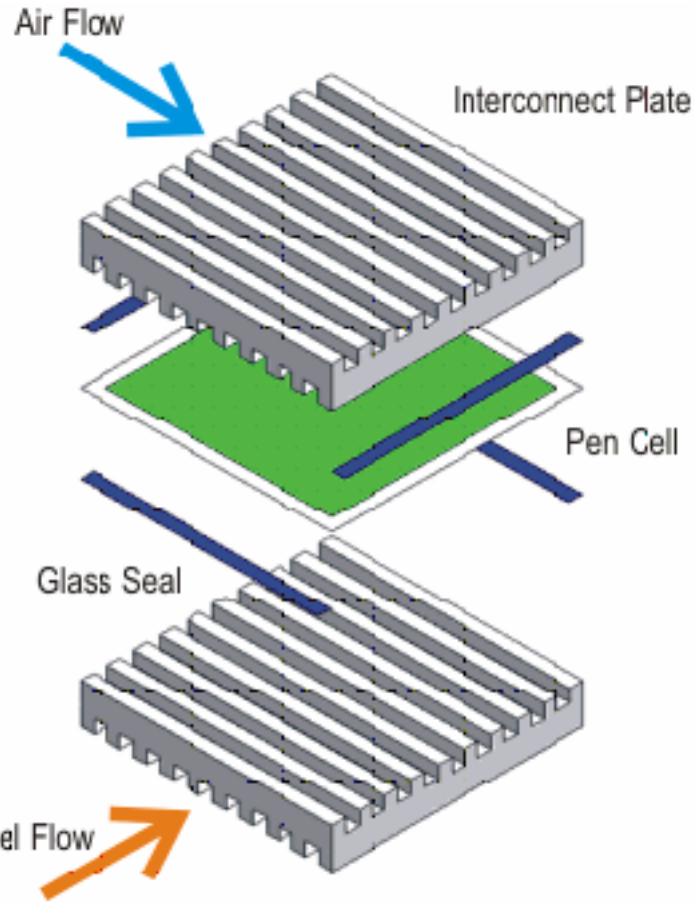
Designing glasses for SOFC seals is a significant challenge

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:

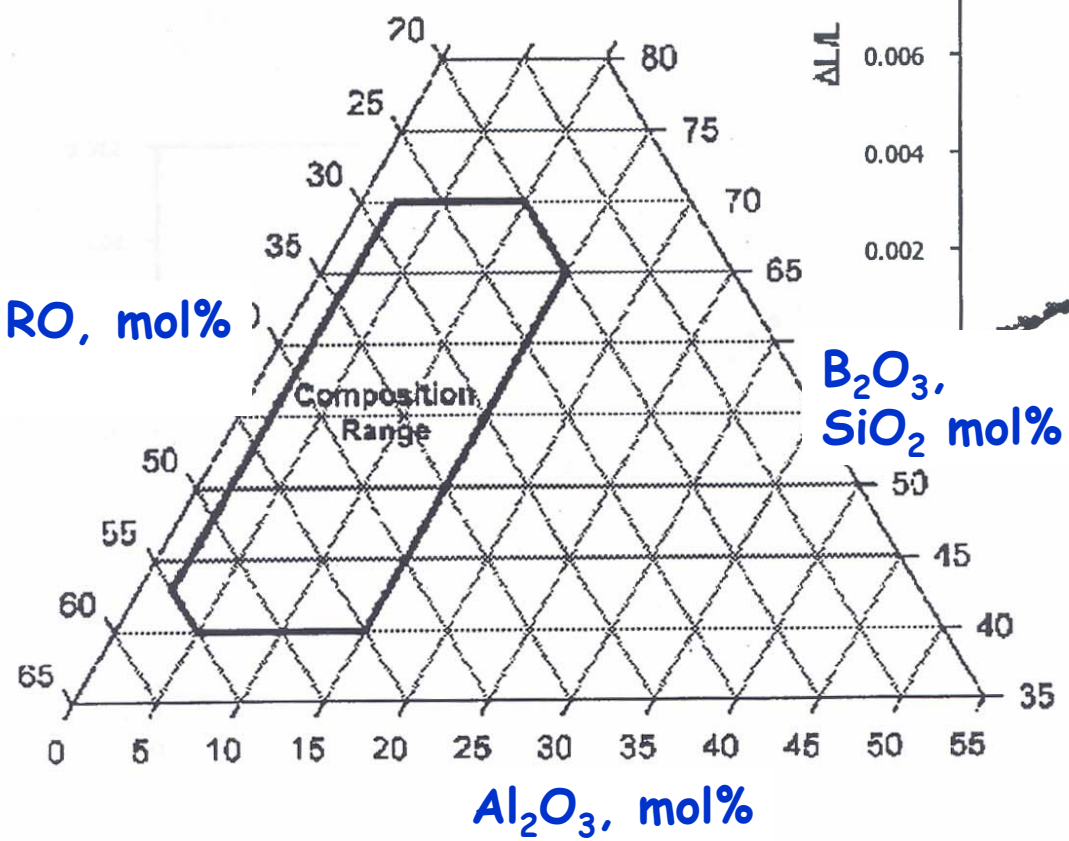
- Thermal expansion matches to a variety of materials
- Relatively high operational temperatures (>700°C)
  - Long lifetimes (>10000's hrs)
  - Maintain stability over range of P_{O2}, P_{H2O}
- Relatively low sealing temperatures (<900°C)
  - Avoid altering other SOFC materials

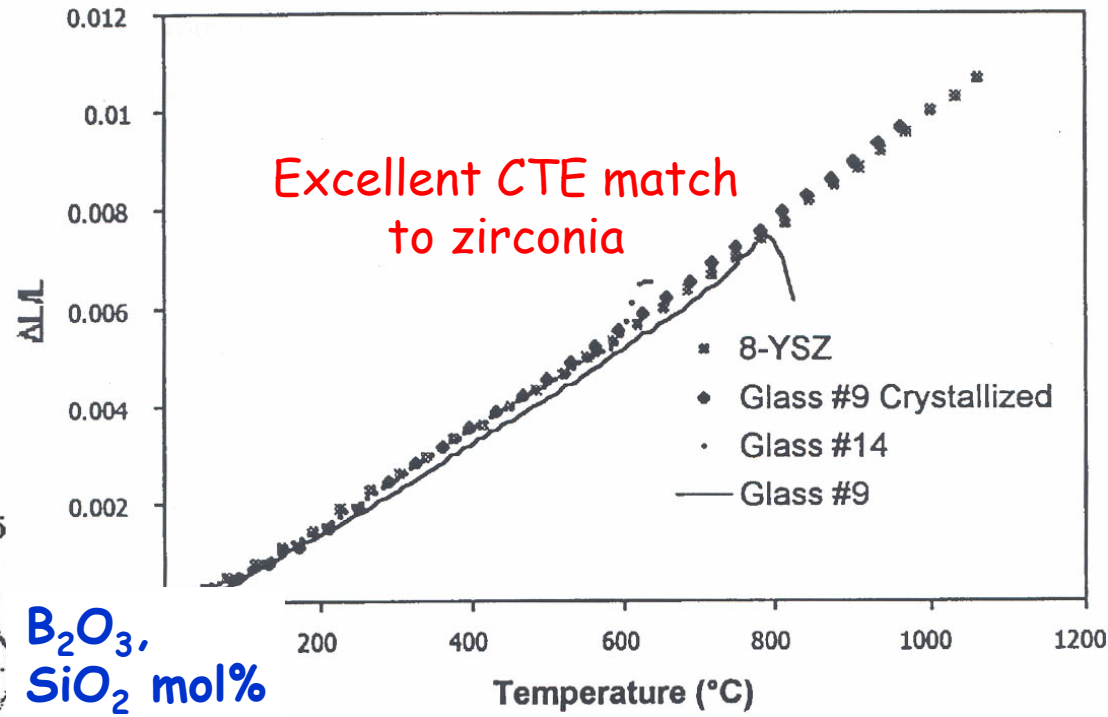


For some designs, glass-ceramics may be suitable

Ba-silicate glass-ceramics have shown promise

Meinhardt, et al., USP 6,532,769
Mar. 18, 2003



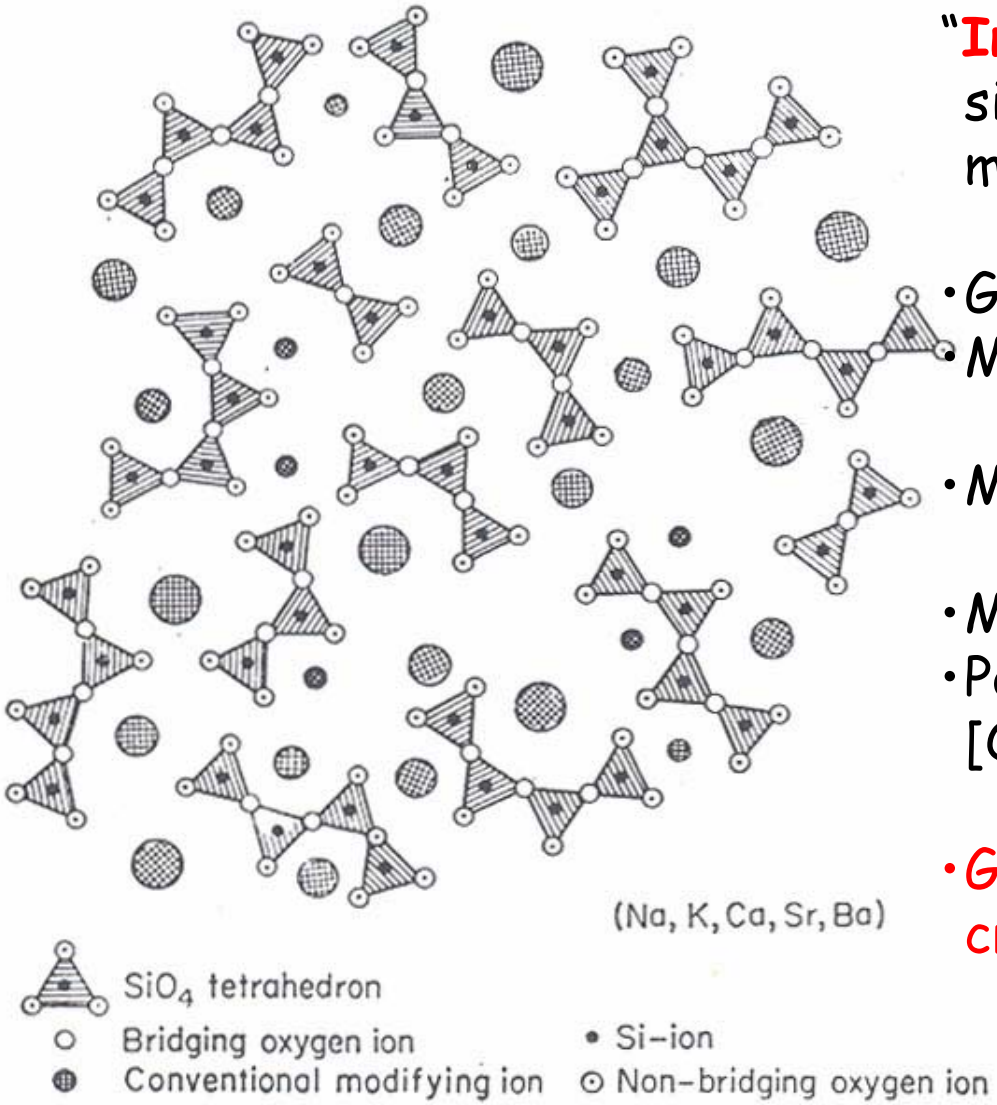


Sealed, crystallized to form high CTE Ba-silicate & Ba-alumino-silicate phases; e.g., $BaO{\cdot}2SiO_2$, $2BaO{\cdot}3SiO_2$

The problem, as seen by 'a glass guy'

1. Challenging compositional design problem
   - Uncommon combination of properties
   - Investigate uncommon families of glasses
2. Glass-ceramics are a likely option
   - Crystallization studies- seal processing and long-term material stability
3. Interfacial chemistry
   - Glass-metal reactions
   - Material stability/volatility
     - Thermochemical stability

Our compositional design is based on unusual glass structures



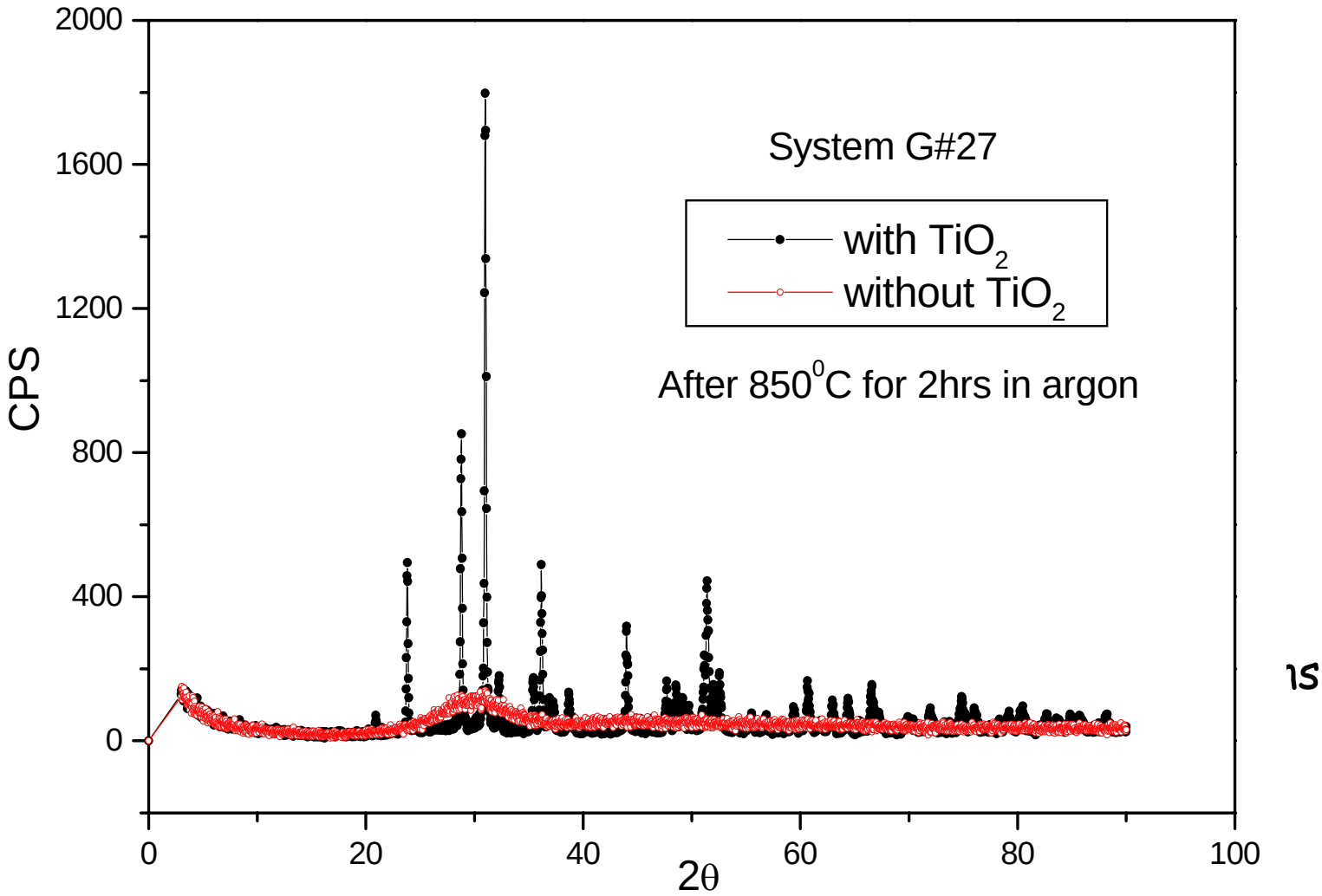
"**Invert Glasses**": discontinuous silicate anions tied-together through modifying cations.

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

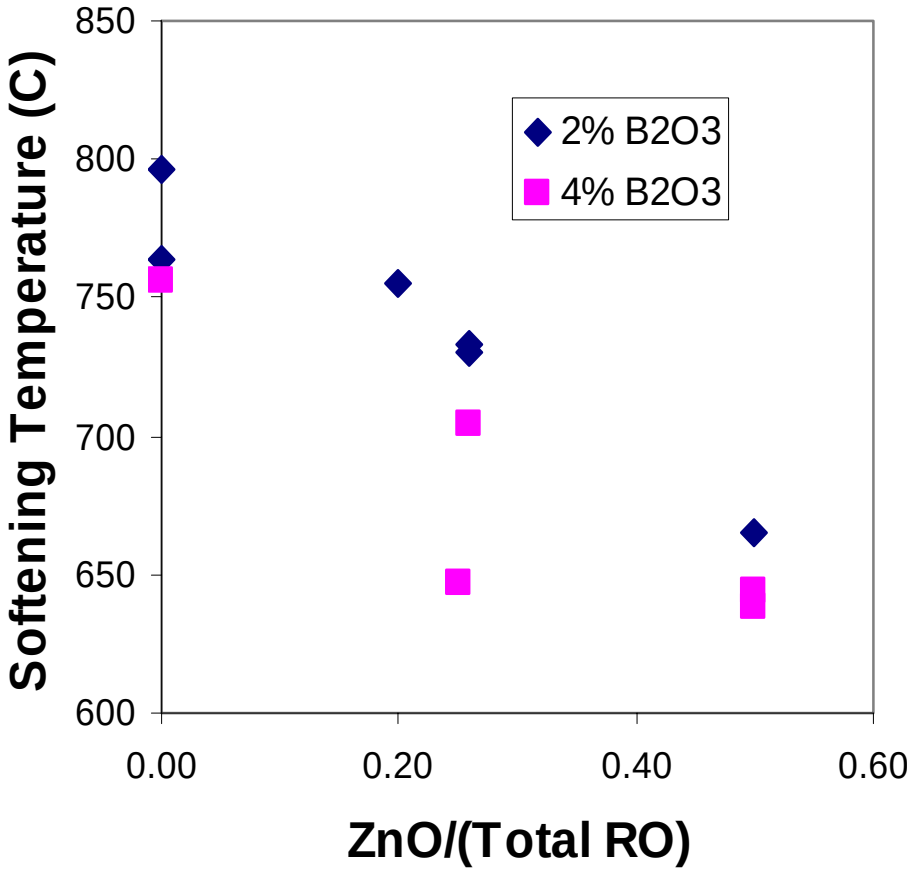
- Metasilicates (chains): [O]/[Si]~3.0
- Polysilicates (short chains): [O]/[Si]>3.0

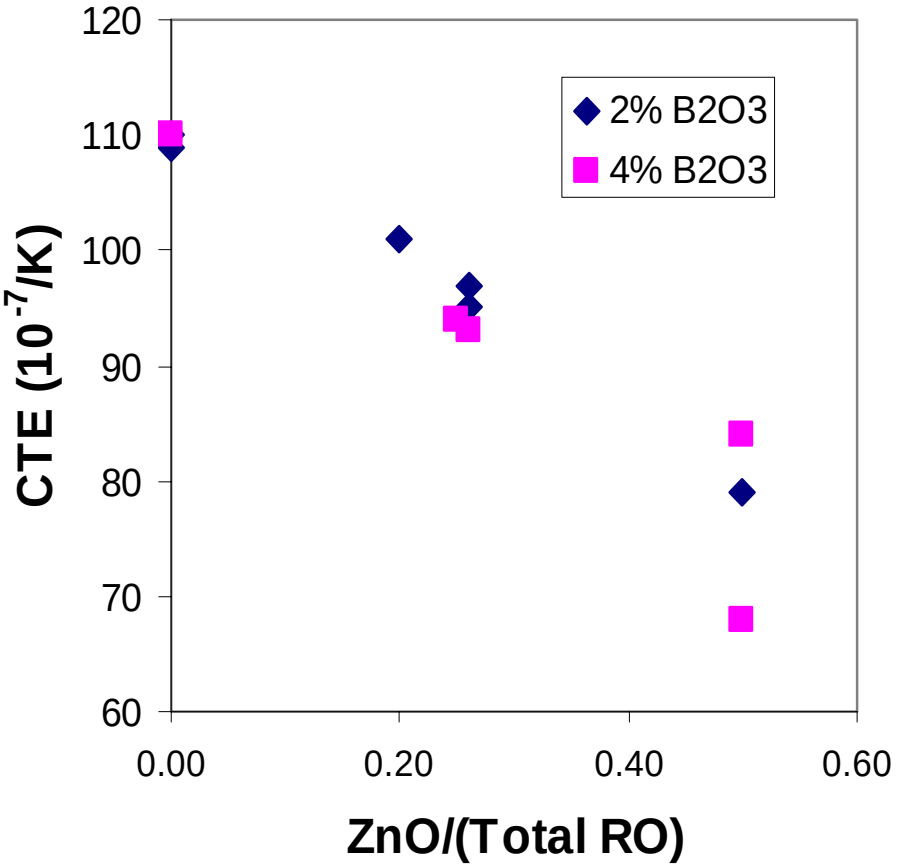
- Greater CTEs from polysilicate crystalline phases

UMR glass-ceramics under development



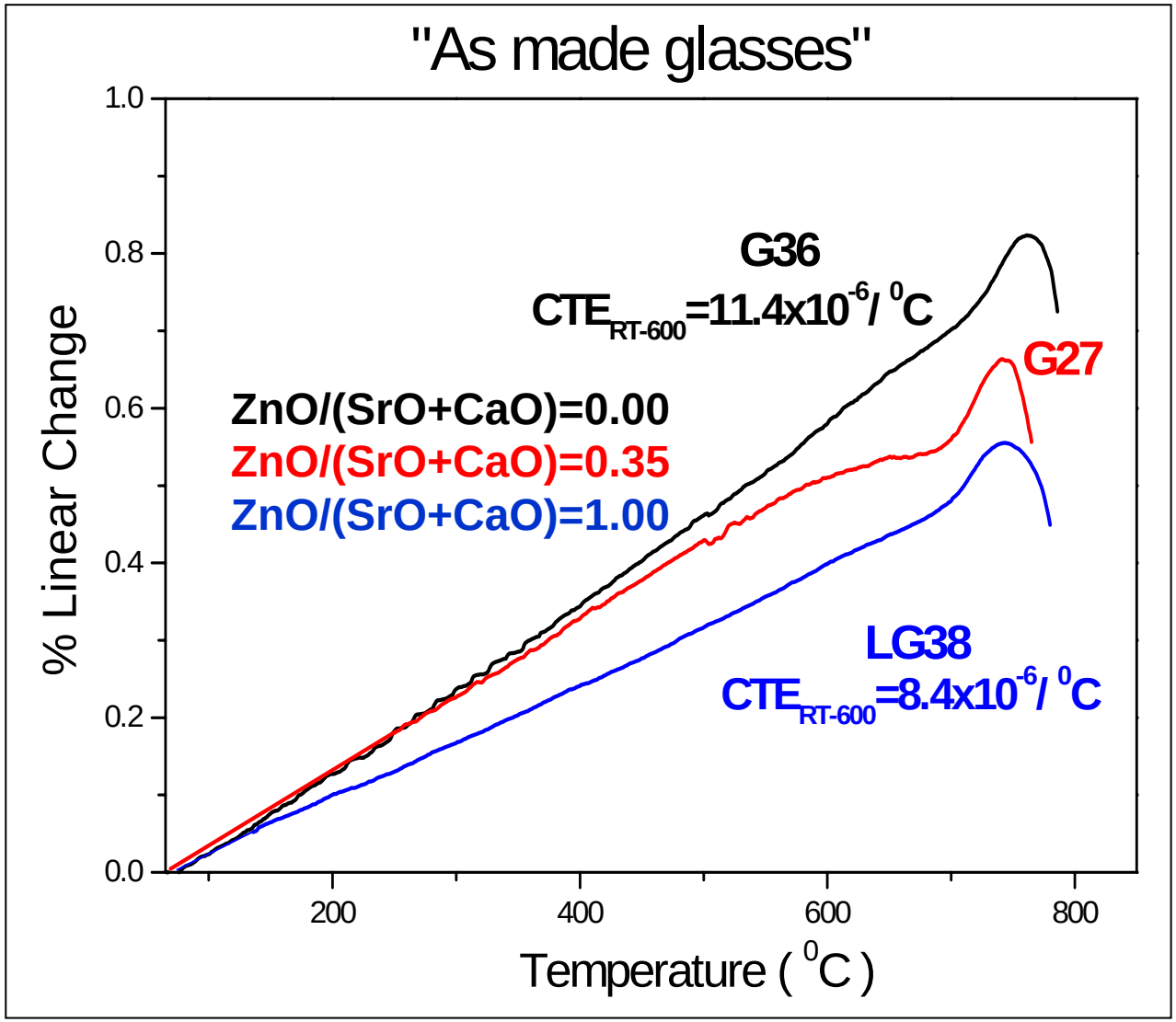
RO-silicate compositions with desirable thermal properties



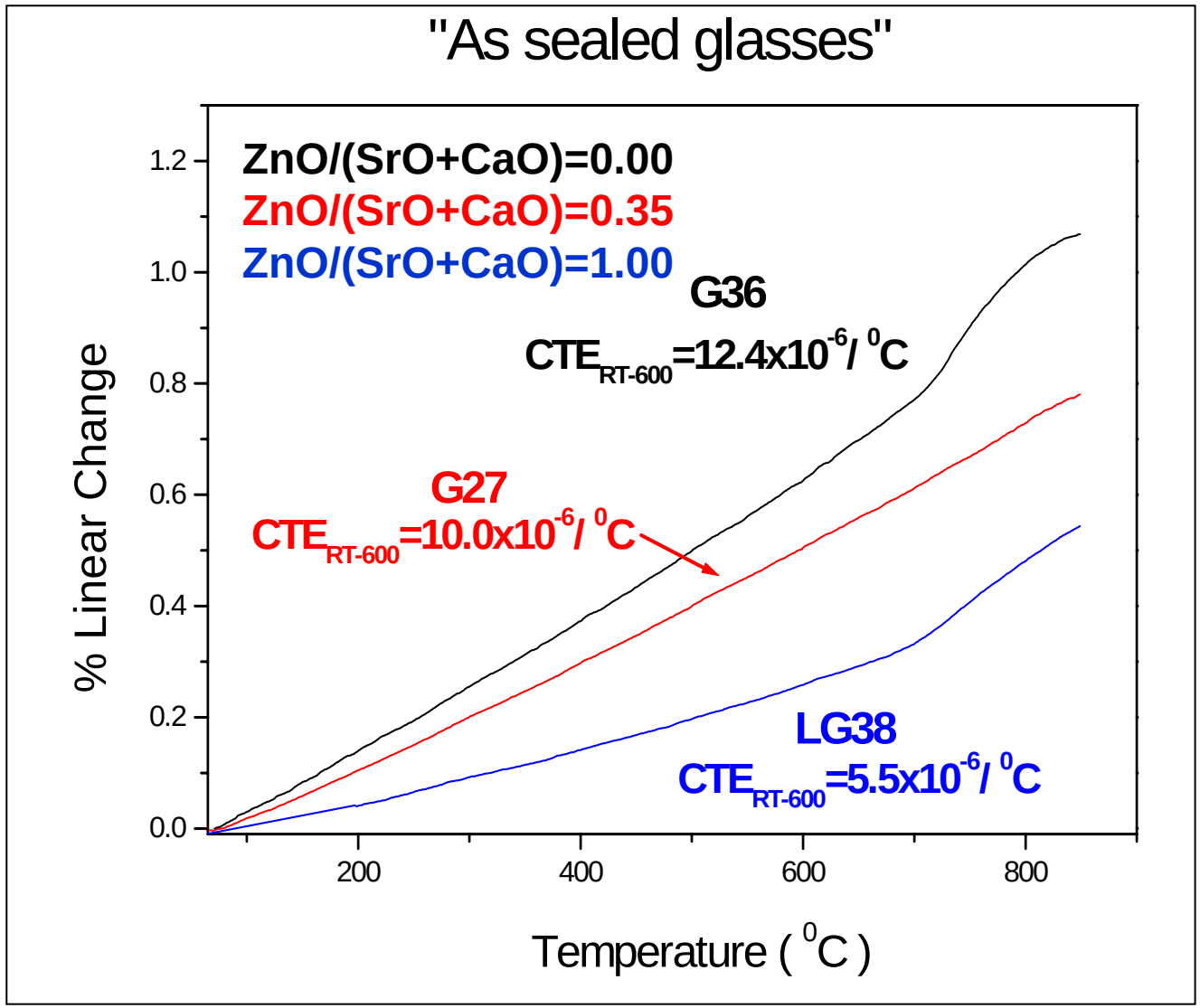


B_2O_3 reduces sealing temperatures and increases residual glass in crystallized samples

Thermal properties of sealing glasses are controlled by the ZnO/RO ratio

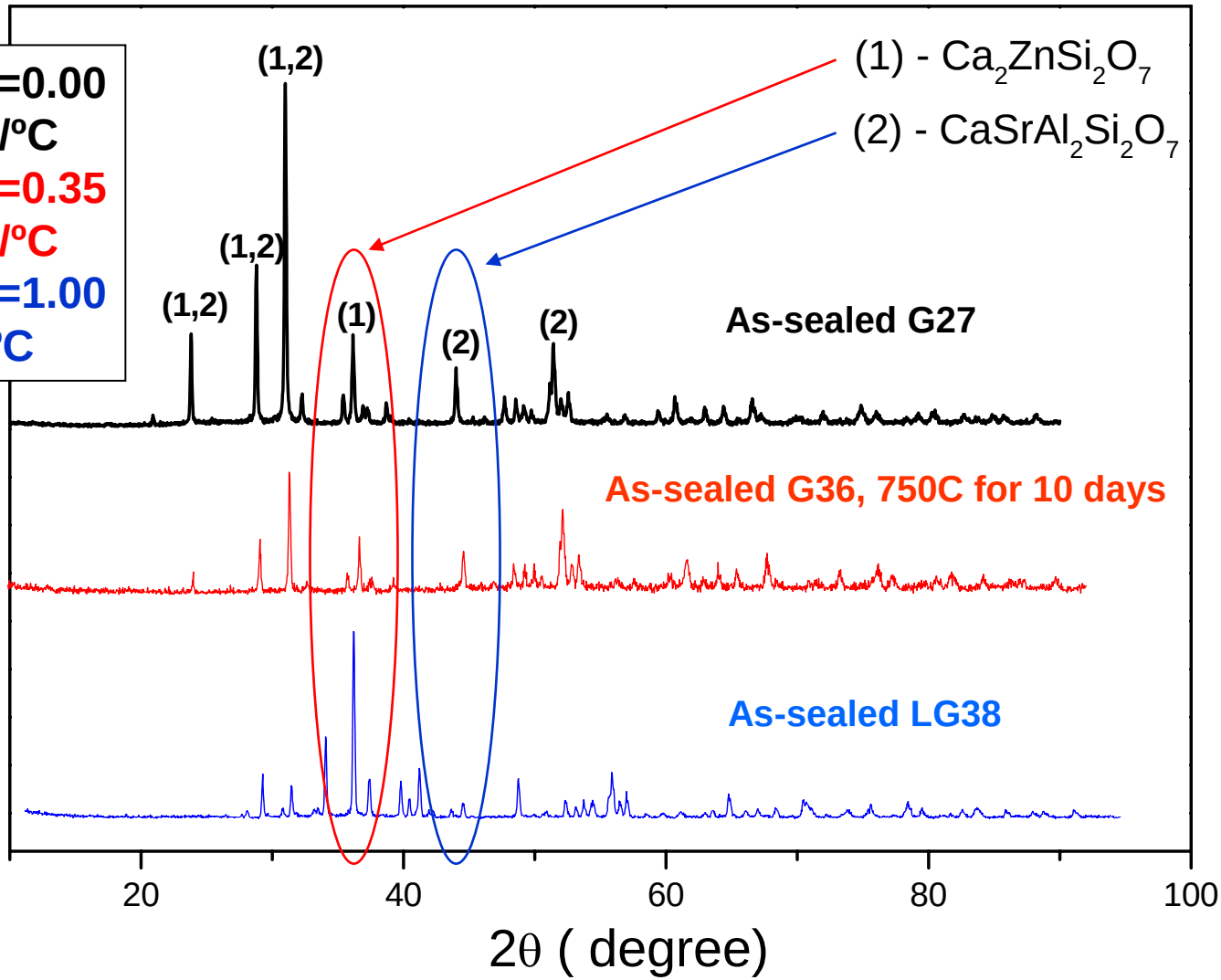


Thermal properties of sealing glasses are controlled by the ZnO/RO ratio



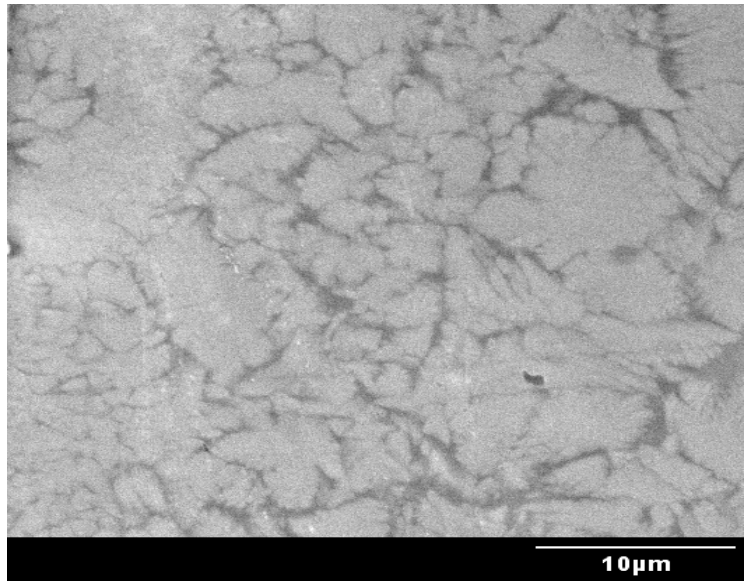
Thermal properties of sealing glasses are controlled by the ZnO/RO ratio

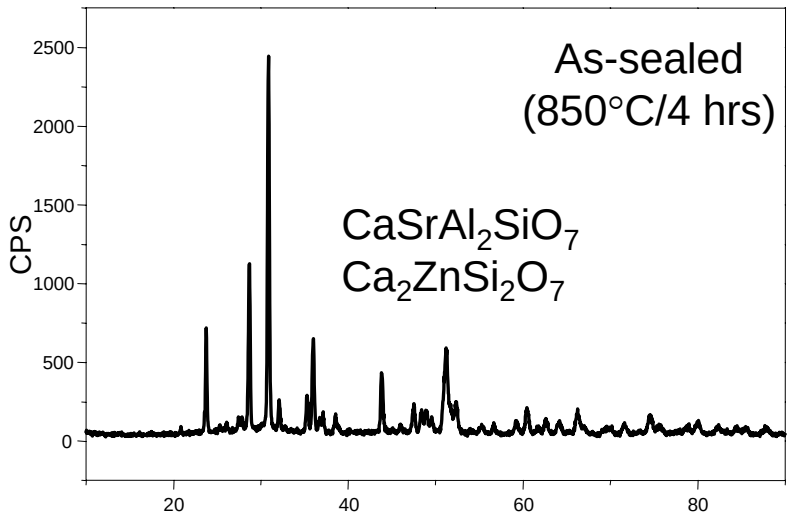
ZnO/(SrO+CaO)=0.00
CTE=12.4 ppm/°C
ZnO/(SrO+CaO)=0.35
CTE=10.0 ppm/°C
ZnO/(SrO+CaO)=1.00
CTE=5.5 ppm/°C

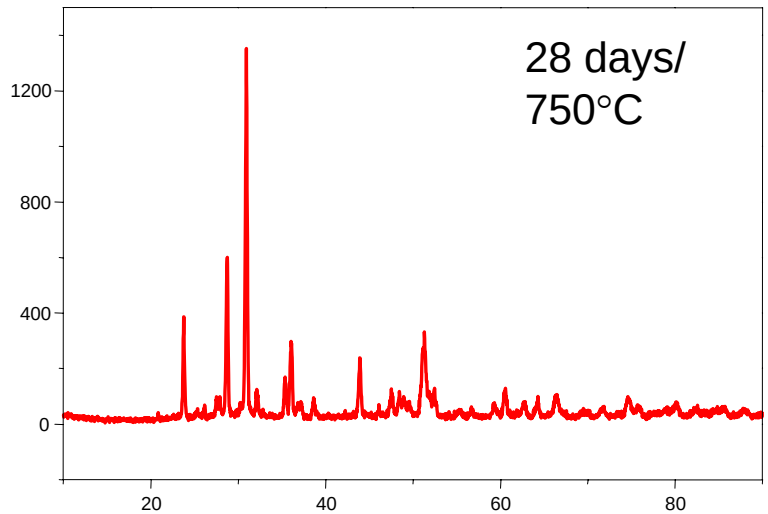


Representative crystalline phases in the UMR glass-ceramics

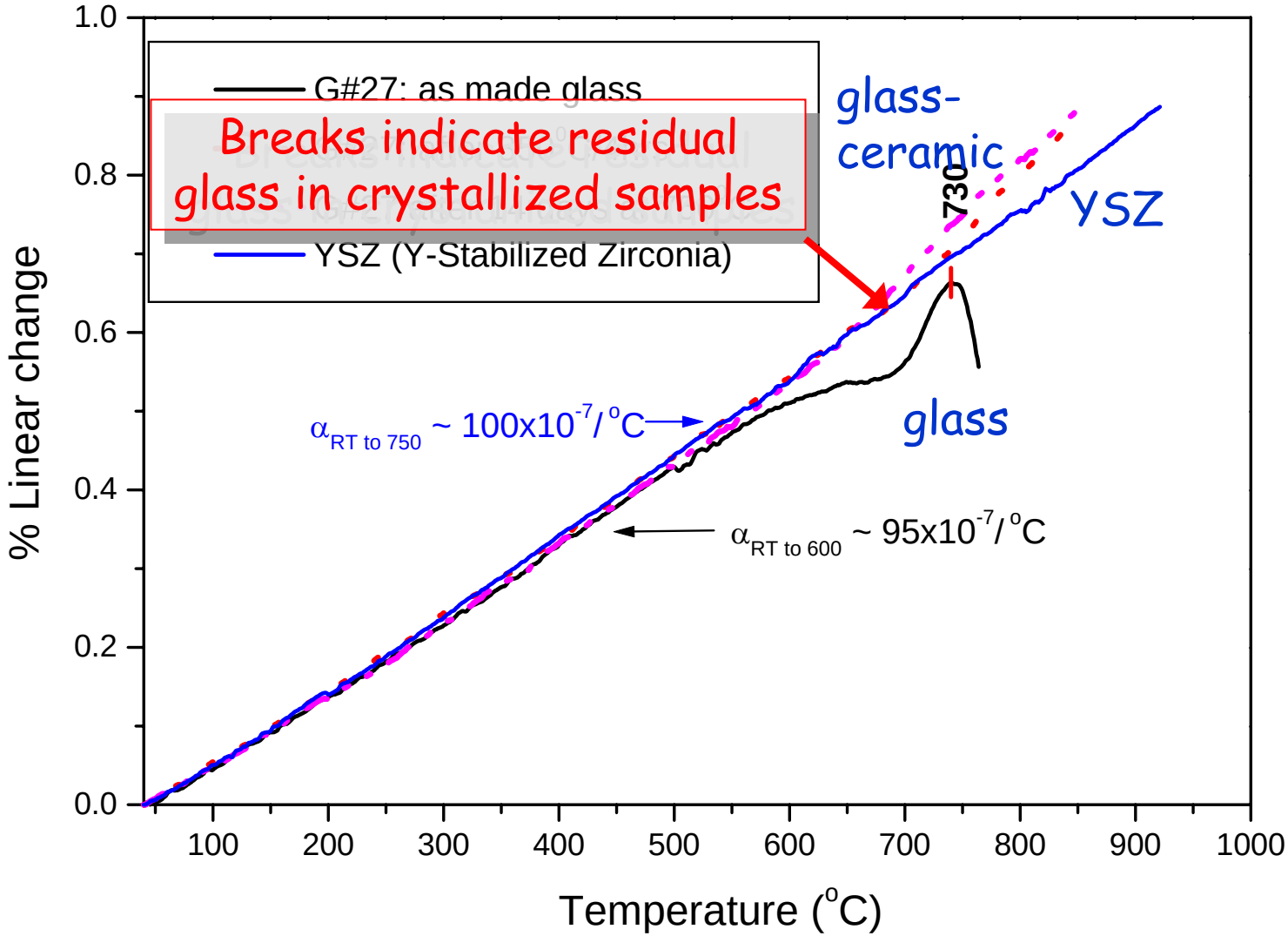
- **Pyrosilicates**
  - $CaSrAl_2SiO_7$, $Ca_2ZnSi_2O_7$
- **Orthosilicates**
  - Sr_2SiO_4, Zn_2SiO_4
- Composition is most important parameter for final phase distribution.







Dilatometry indicates good CTE-match with YSZ



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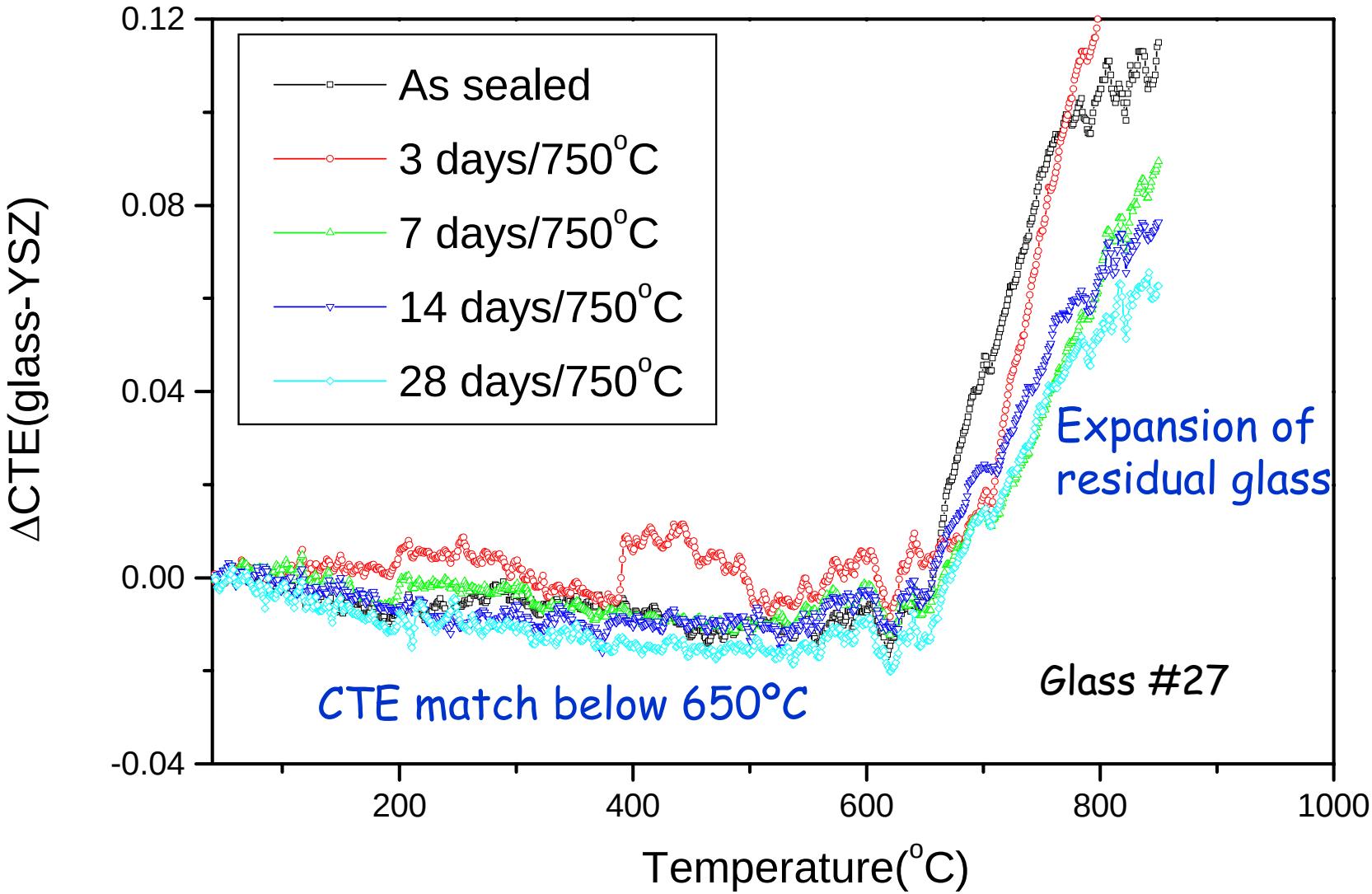

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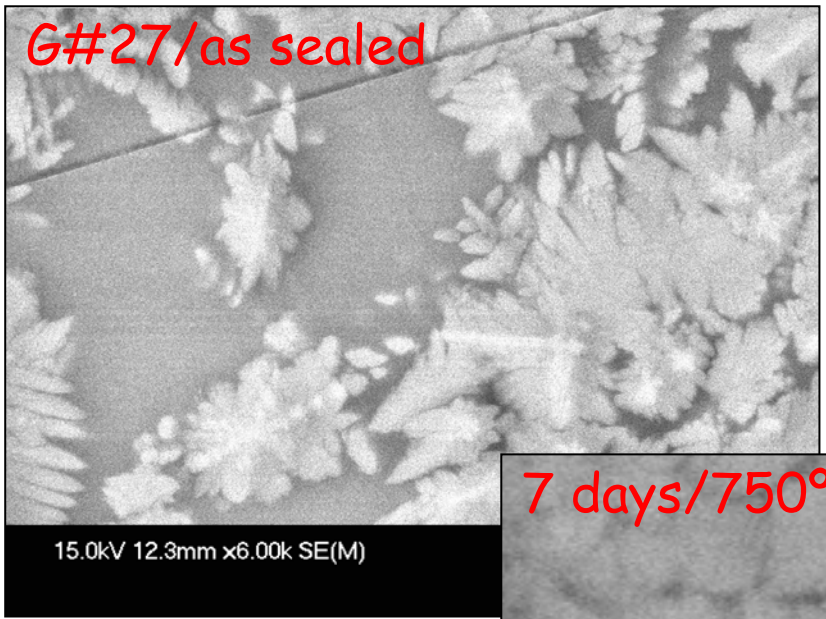
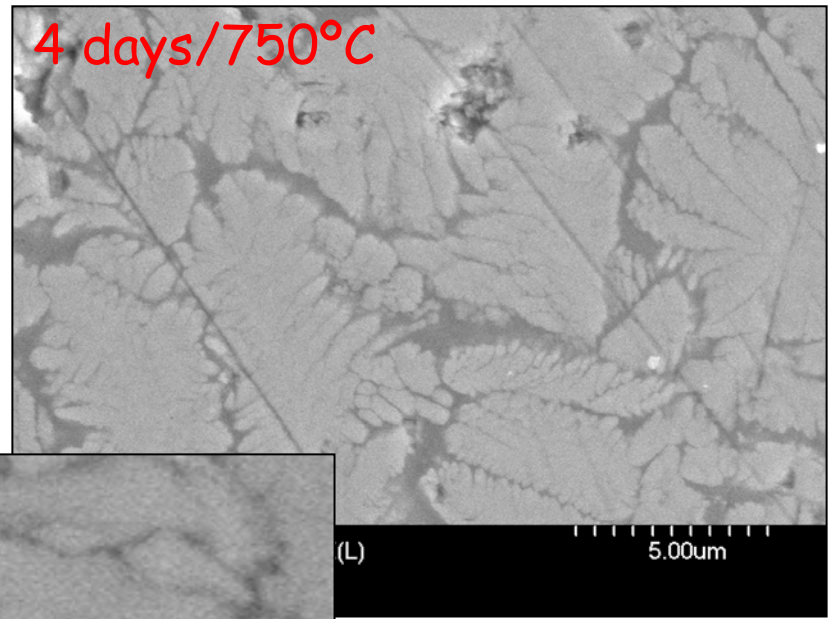
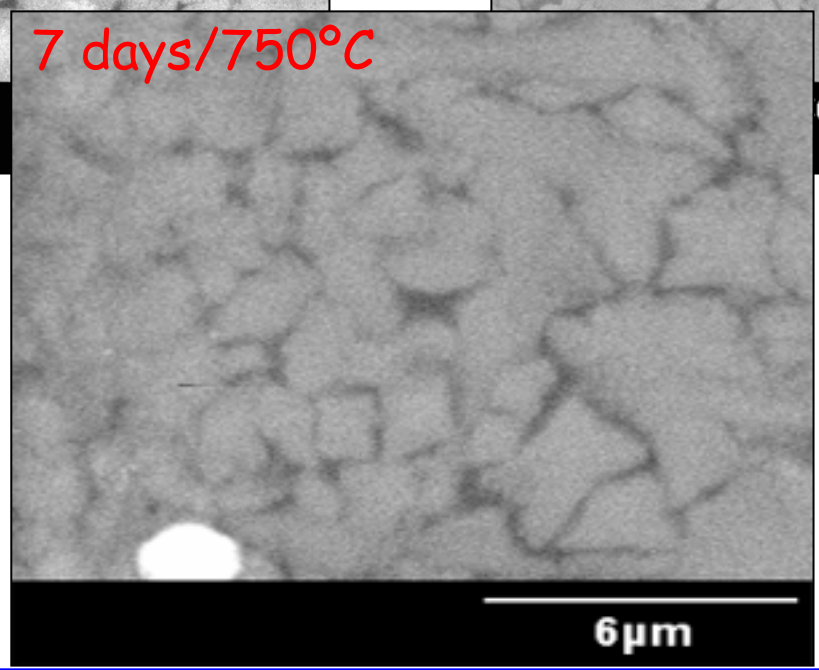
Glass-ceramic microstructure evolves with time

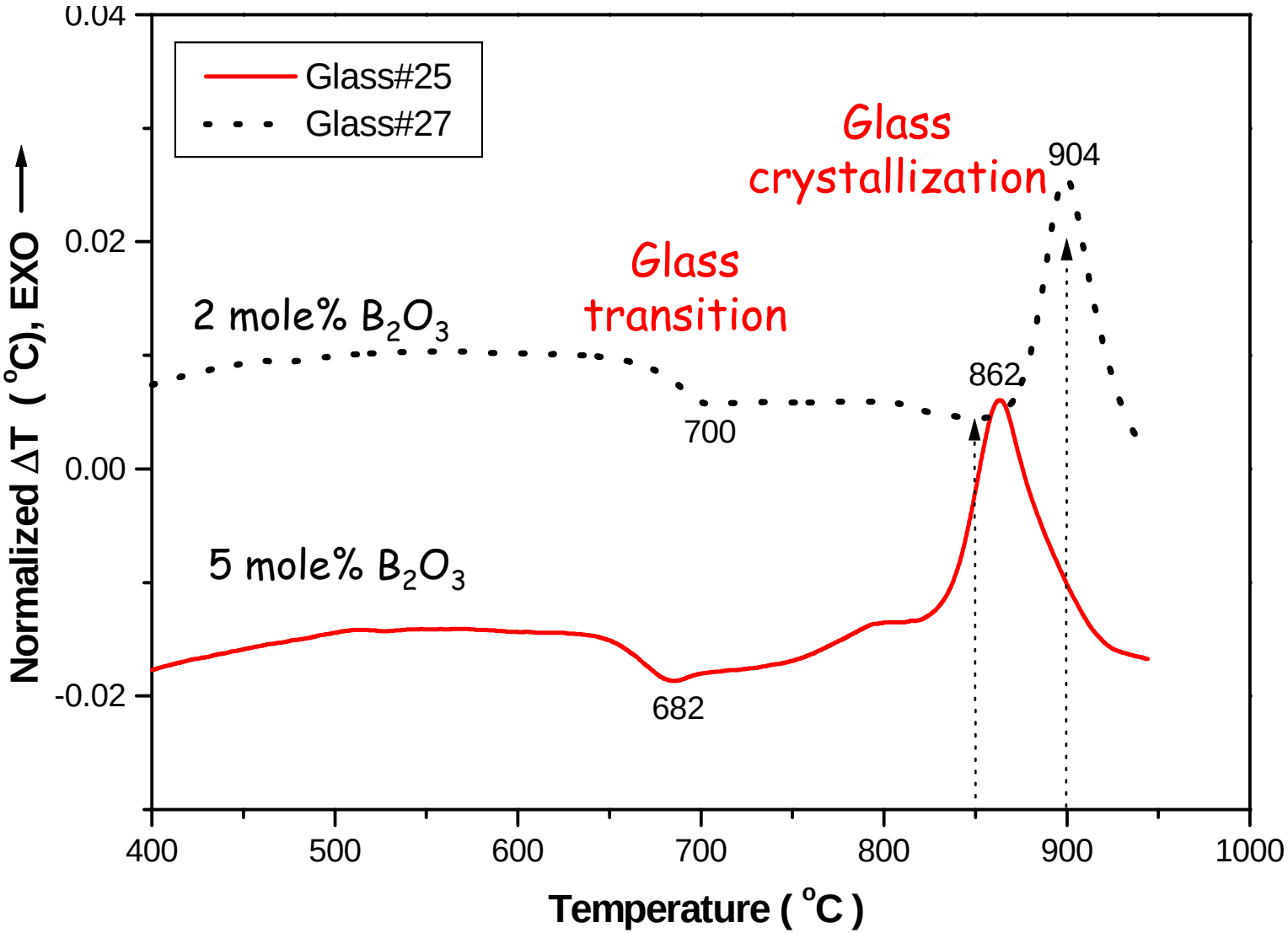




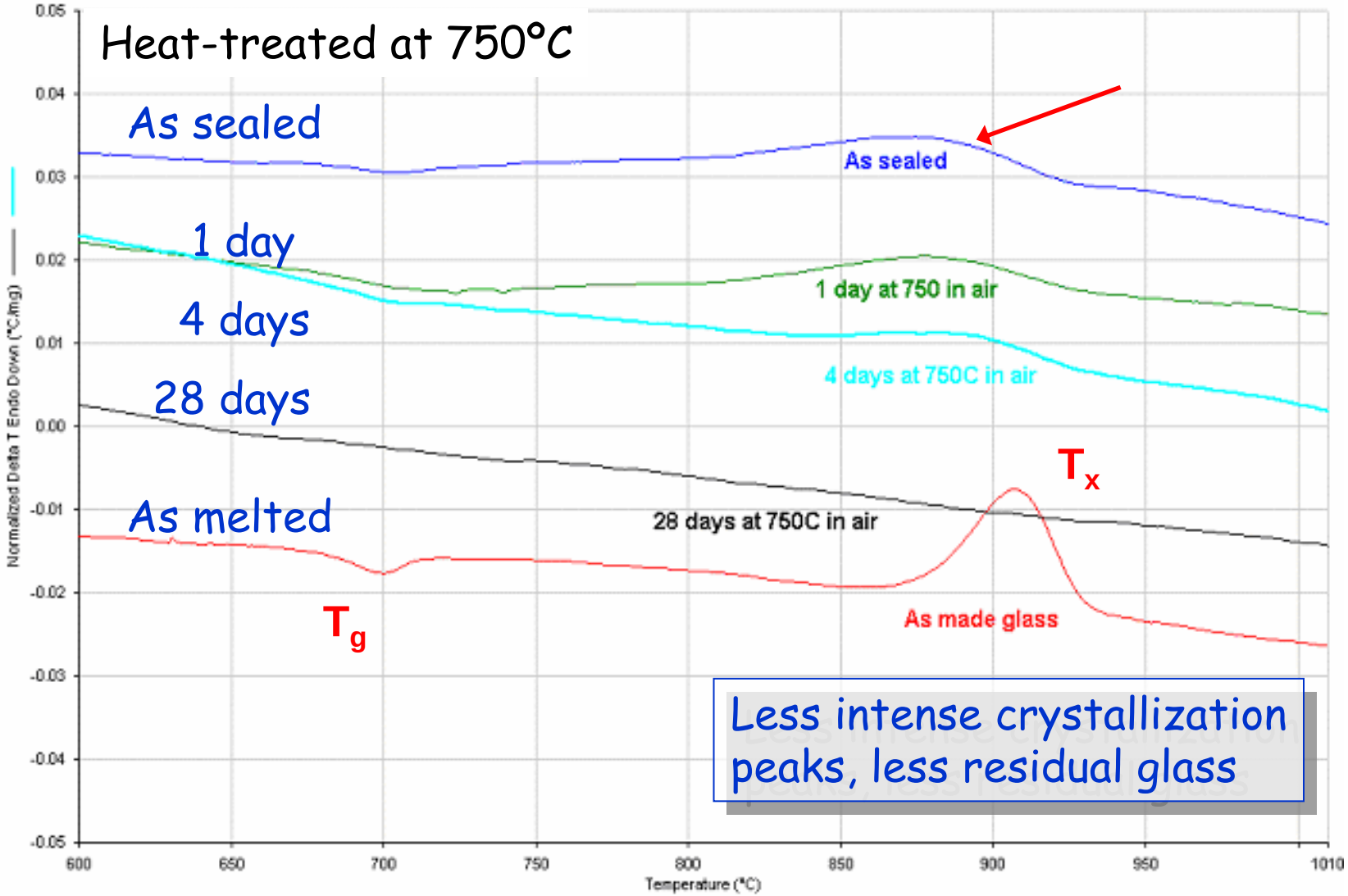


Residual glass crystallizes with time

DTA provides information about sealing glasses

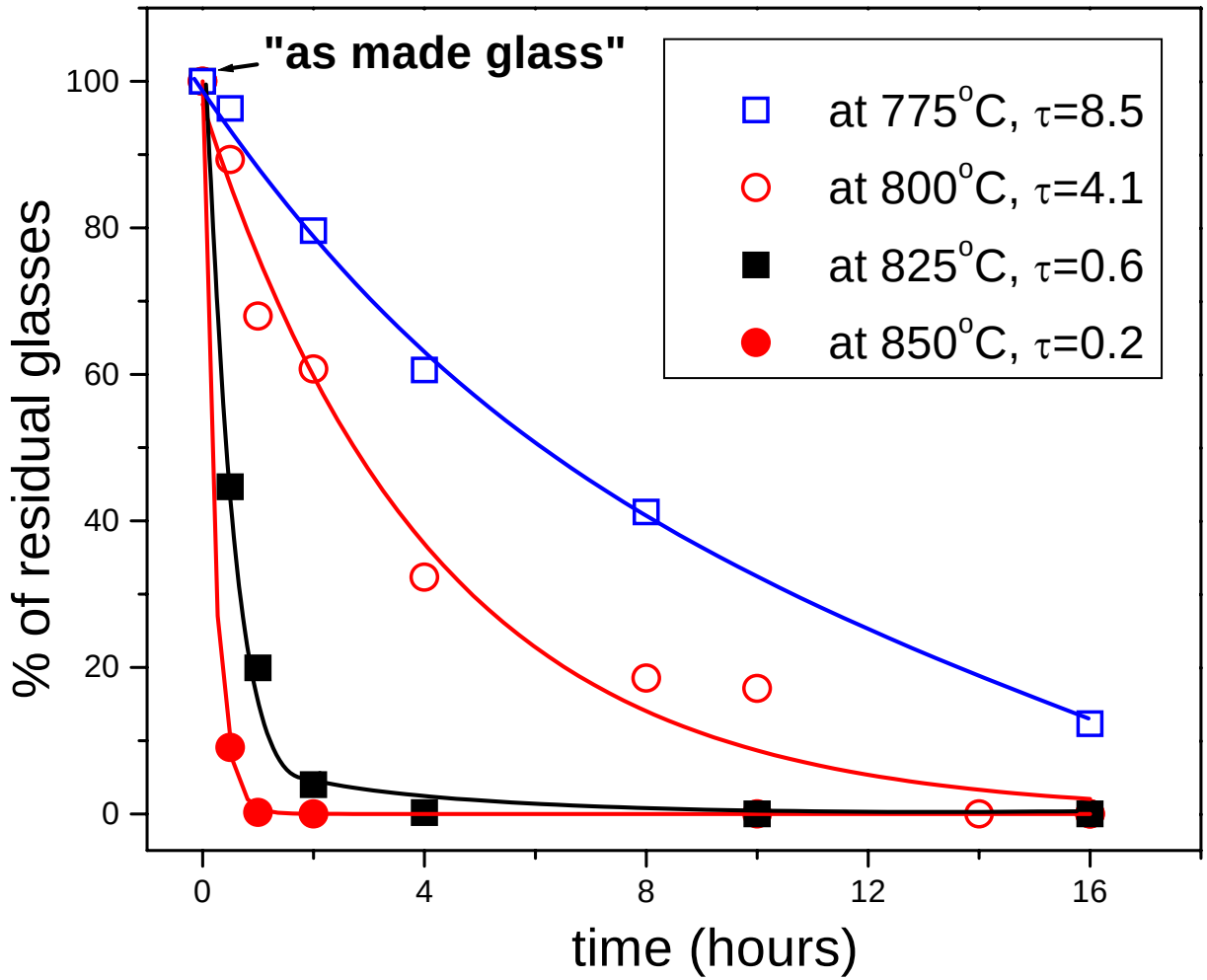


DTA provides information about the nature of the residual glass



DTA results are used for crystallization kinetic studies

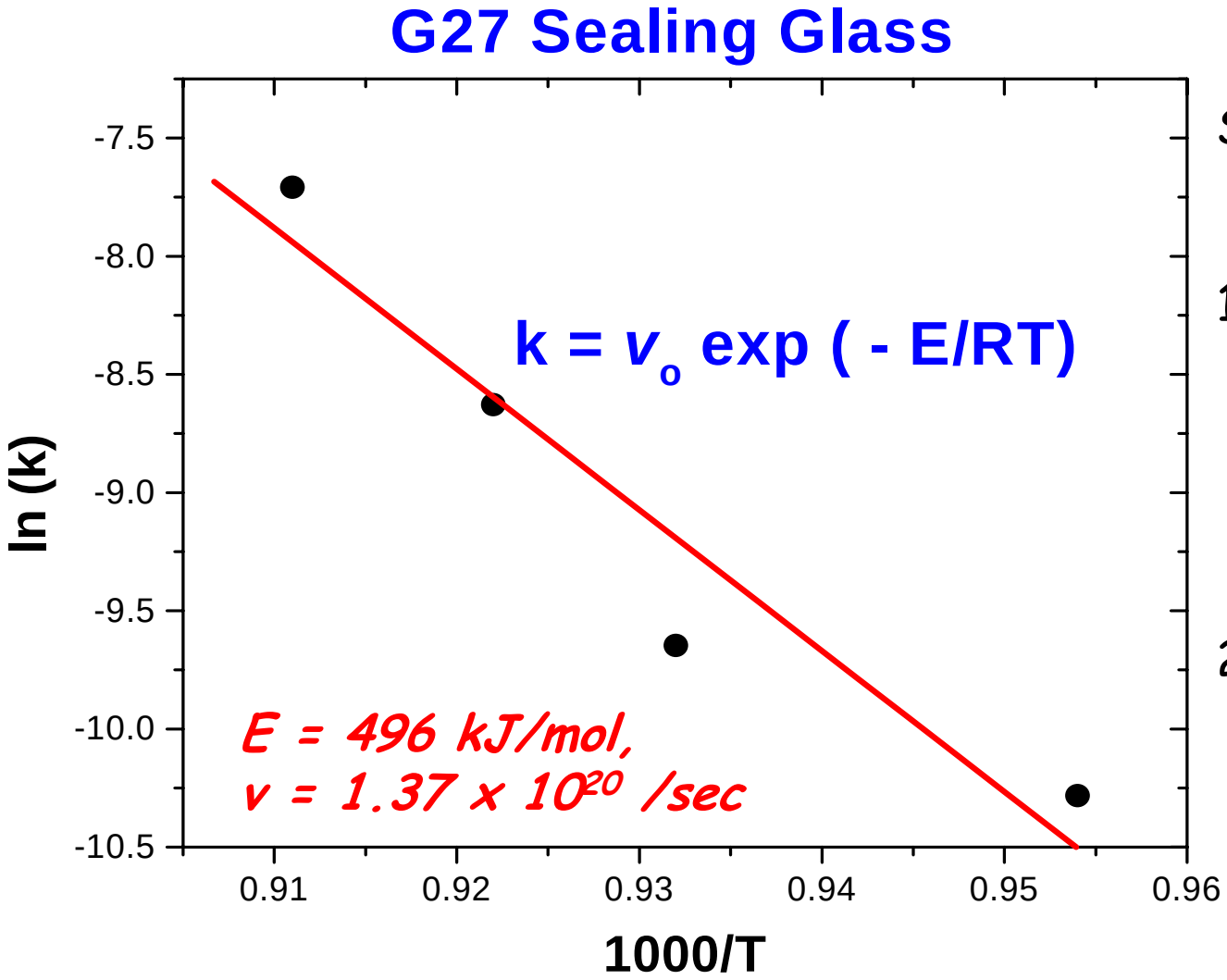
G#27 sealing glass treated in air



Avrami equation:
$(1-x)=\exp(-Kt^n)$;

n=1: surface crystallization

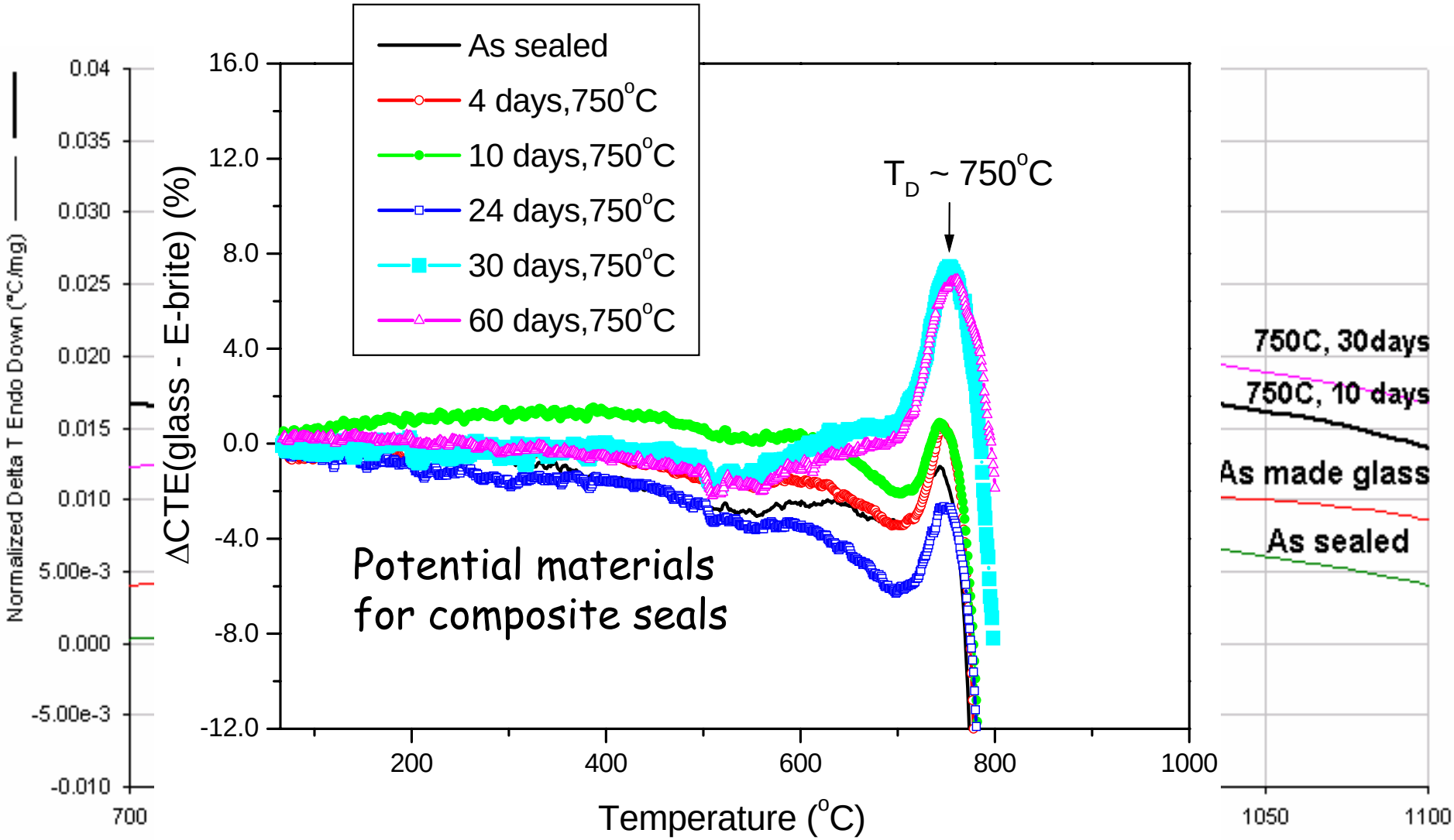
DTA results are used for crystallization kinetic studies



Studies are presently underway to:

1. Characterize the effects of nucleating agents on crystallization kinetics
2. Develop compositions less prone to crystallization

Glass #36 is less prone to crystallization at 750°C



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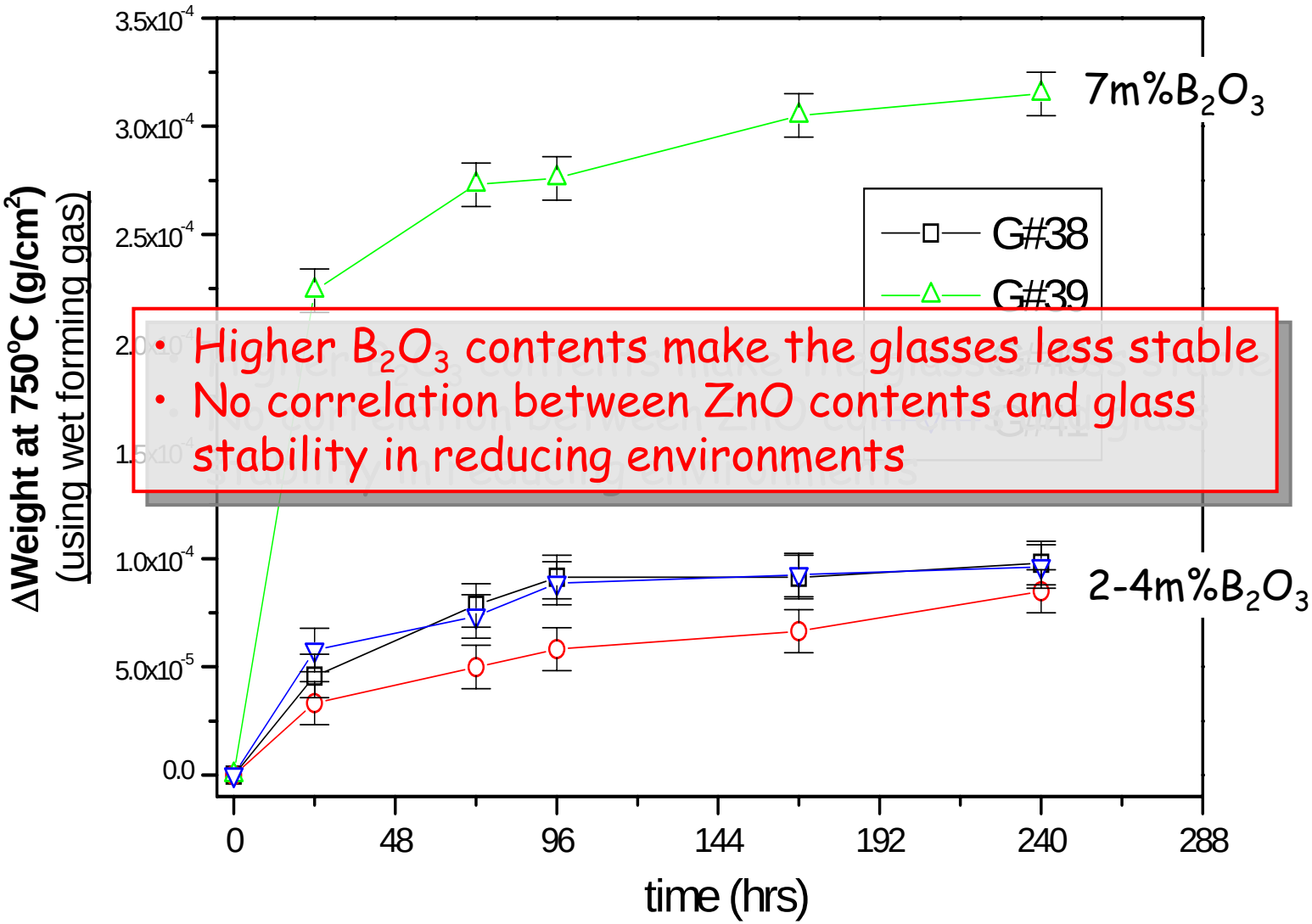
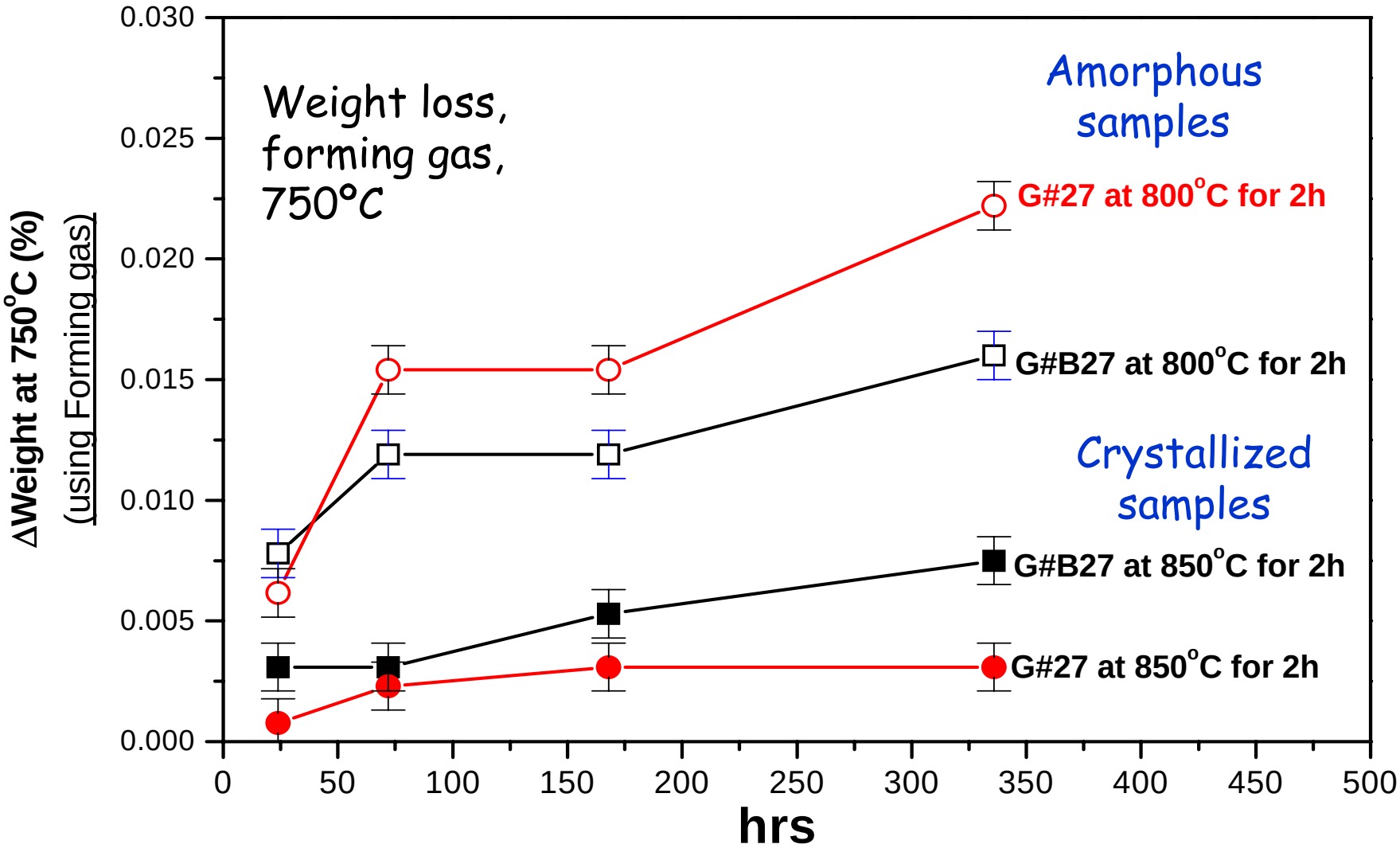
Glass stability in wet forming gas has been evaluated

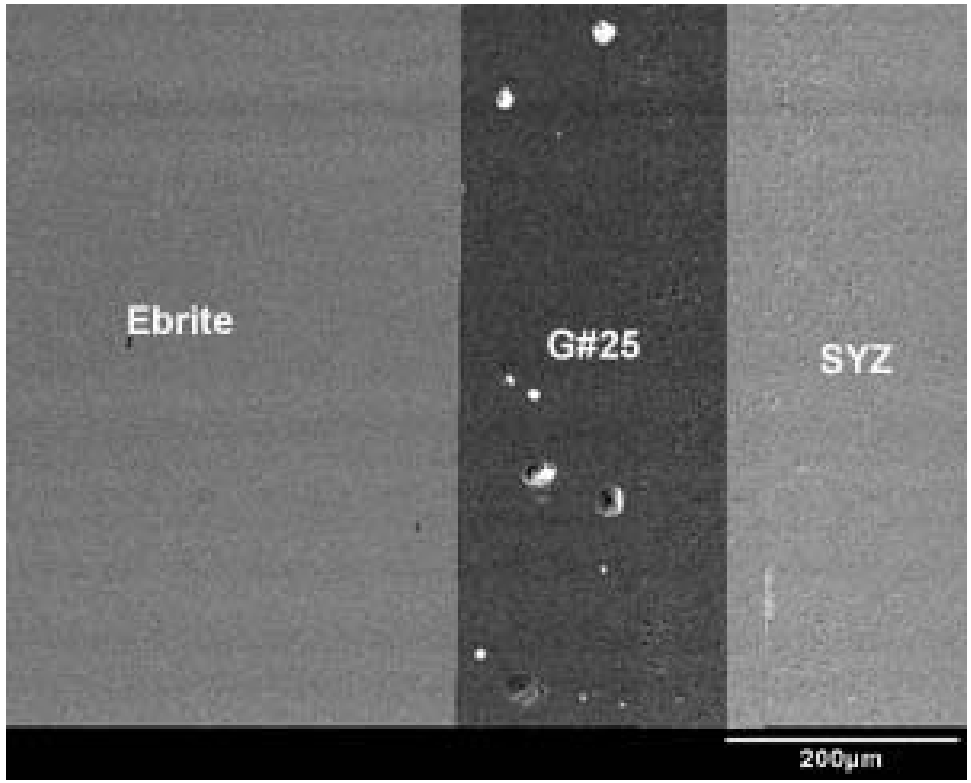


Glass-ceramics are more stable in forming gas than glasses



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

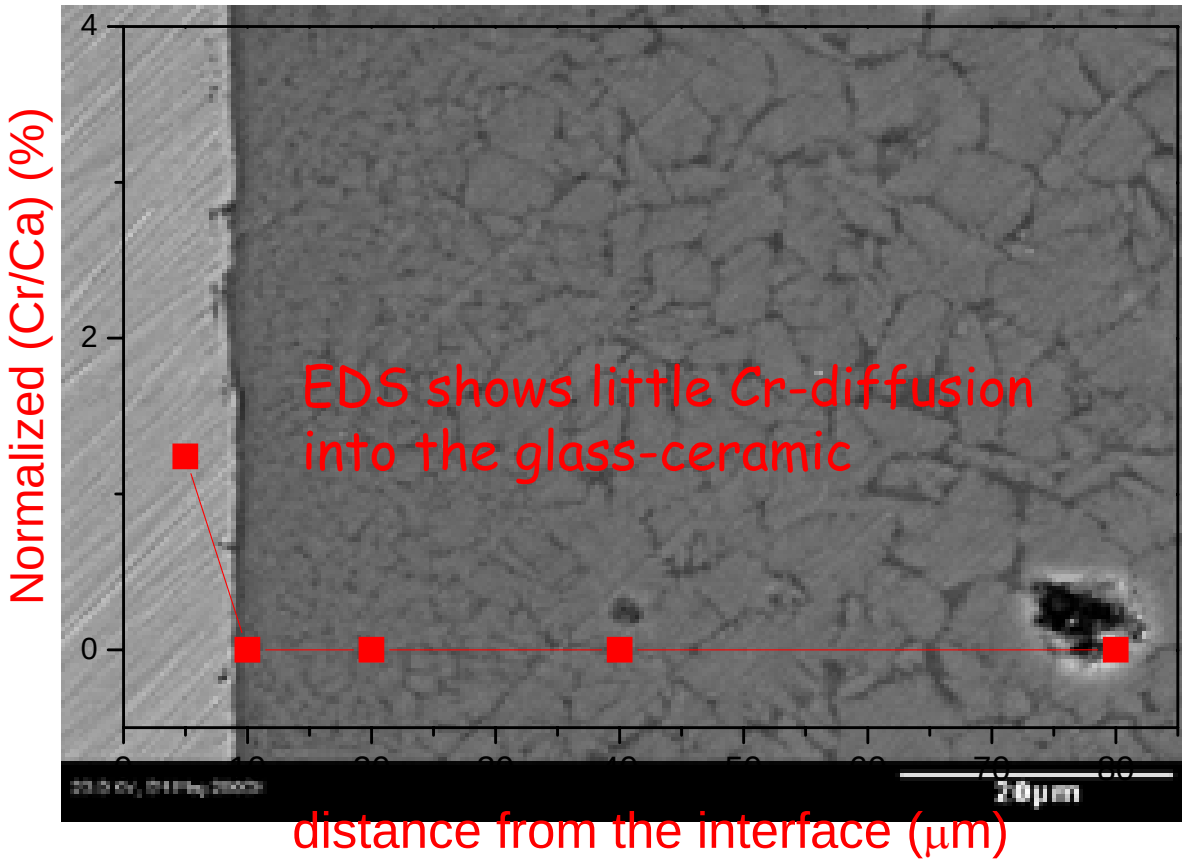


"As sealed" Glass 25 paste with YSZ and E-bright substrates (850°C/4hrs, Ar

Test seals have been prepared with SOFC coupon materials

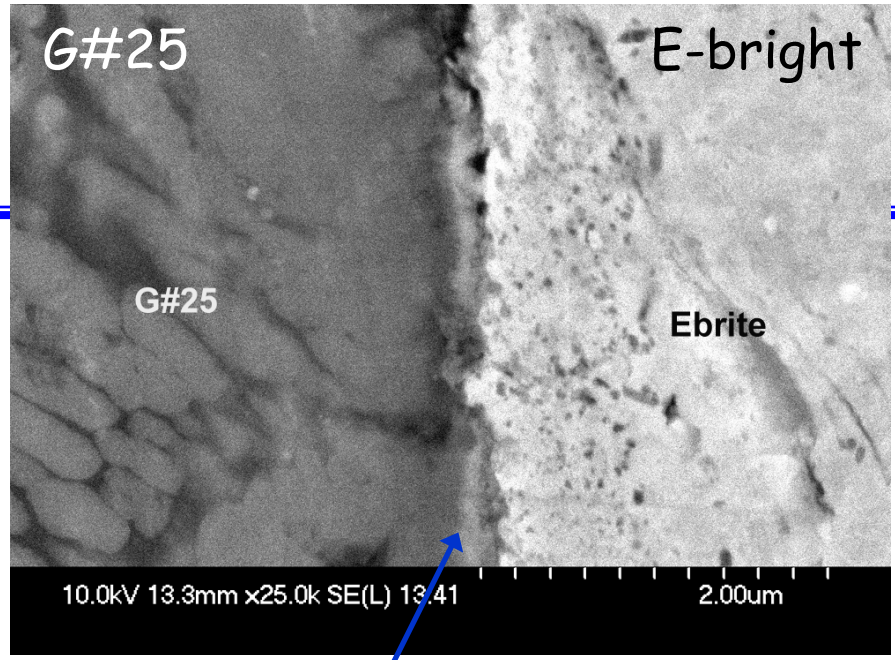
- Glass pastes
  - Glass powders, ~25μm
  - Interconnect alloy: Crofer
  - Cr-ferritic steel
  - CTE ~ 11.9 ppm/°C

  After sealing:
  - Glass-ceramic thickness: 100-200μm

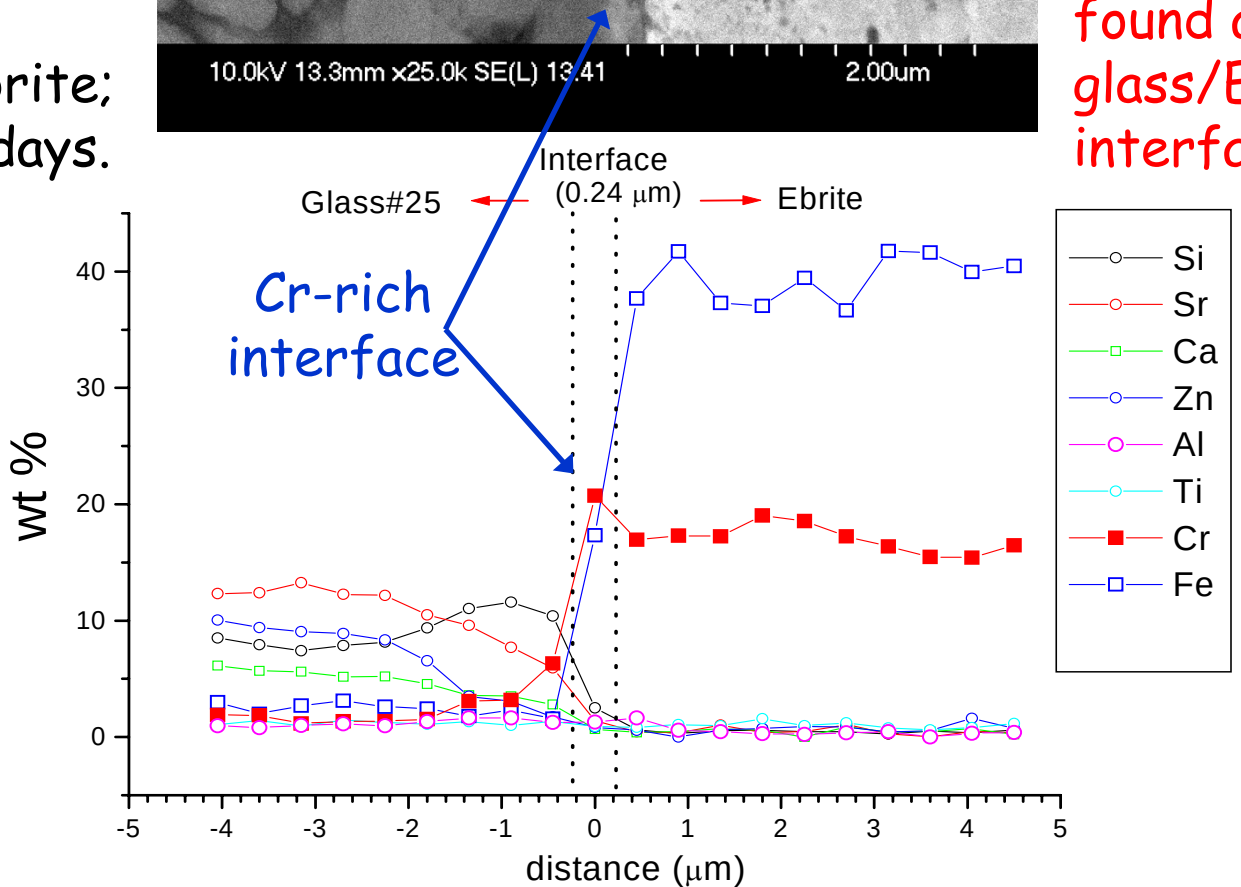


Glass 27 with Crofer APU22 after four days at 750°C in air

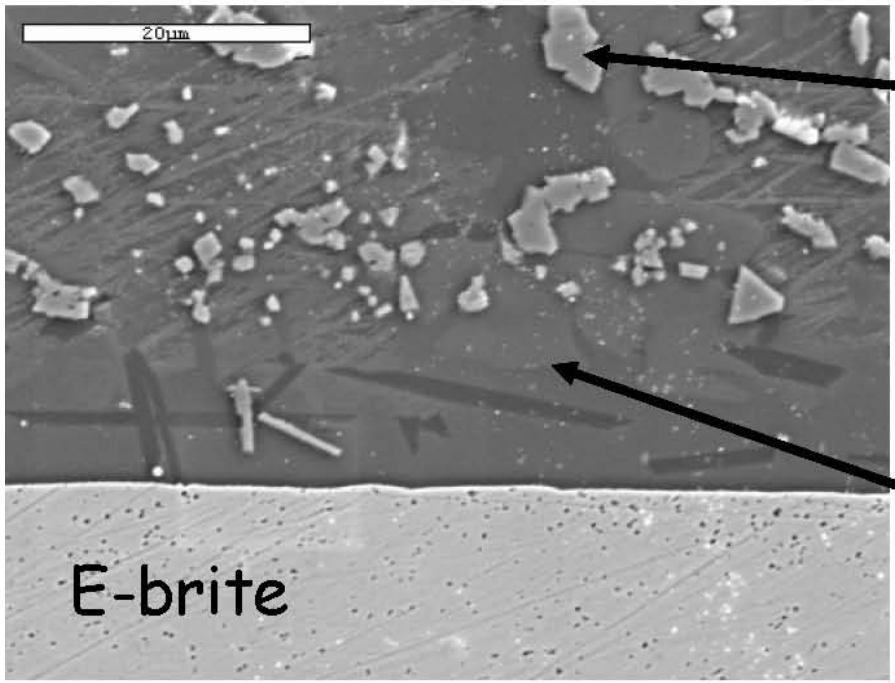
Glass#25/E-brite; 750°C for 14 days.



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

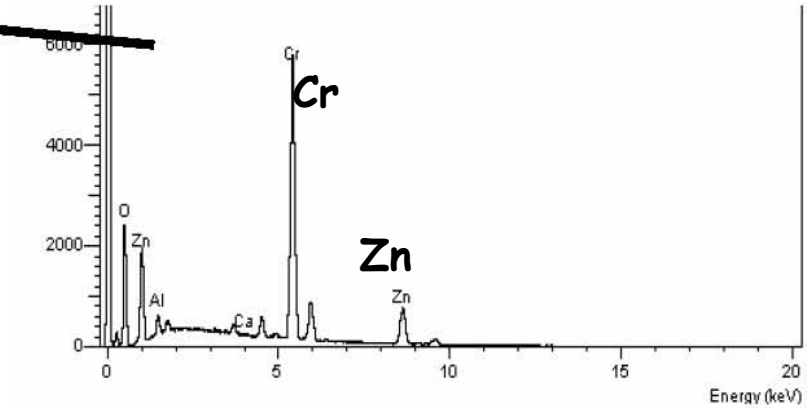


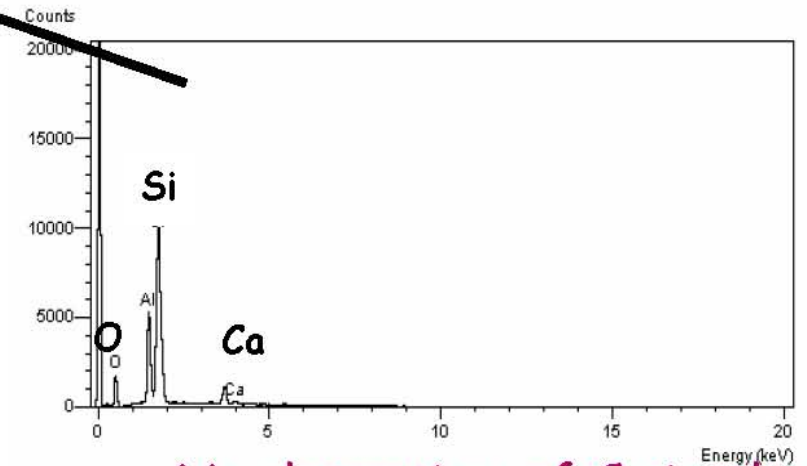
Glass #27 reacts with E-brite alloy at 950°C



After sealing cycle of 10 min @ 950°C

Precipitates contain Zn, Cr, Al, and O



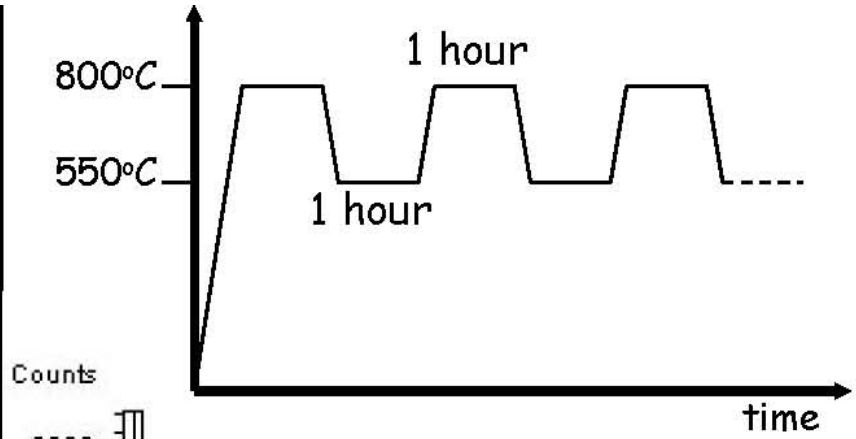


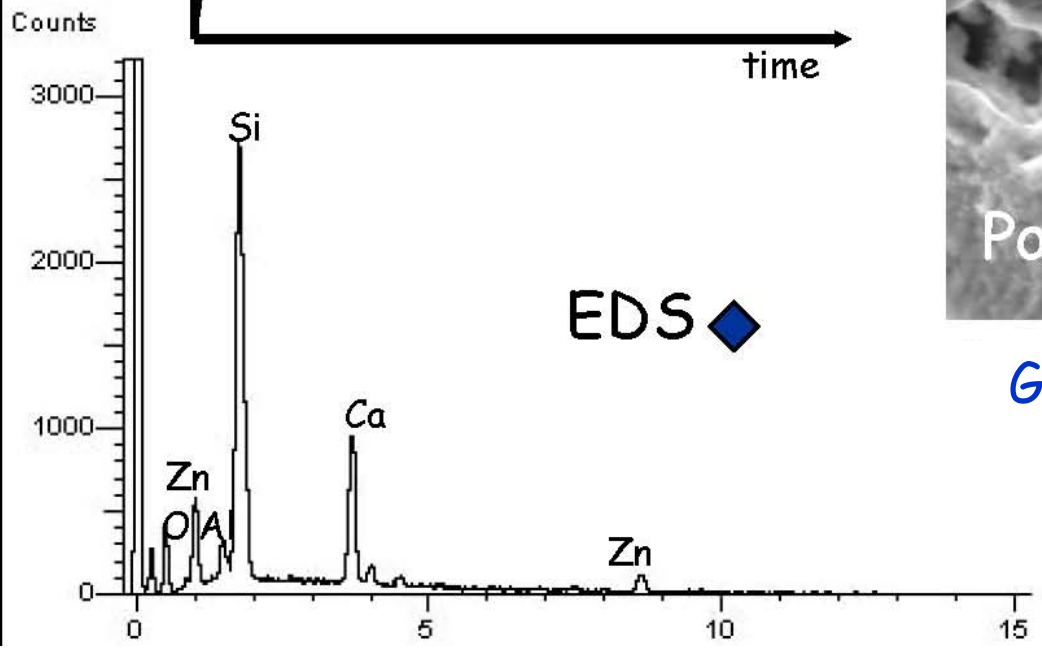
No detection of Cr in the glass matrix

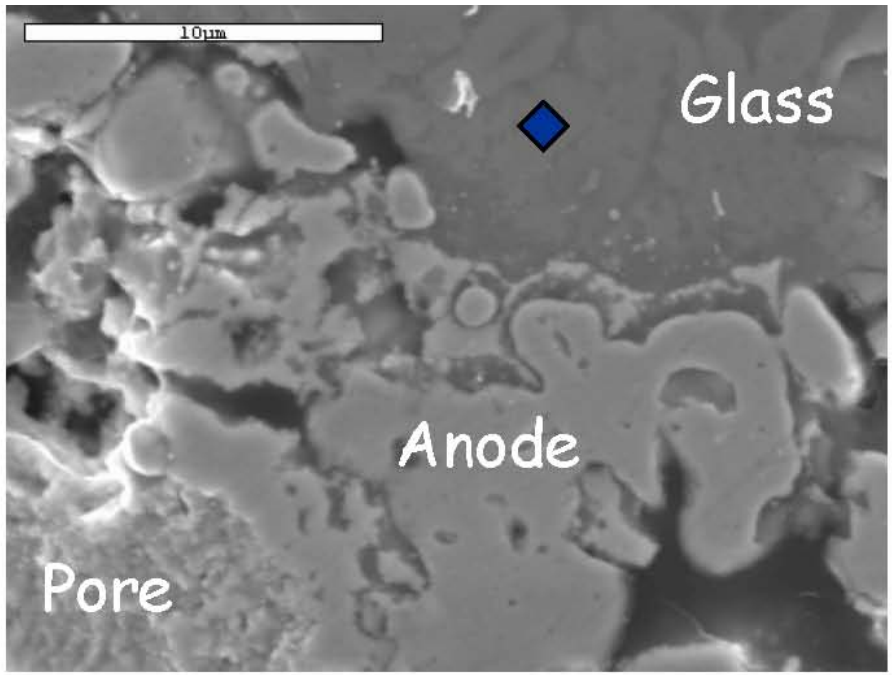
From Ron Loehman, Sandia

Sandia National Labs - Advanced Materials Laboratory

The glasses do not appear to react with anode materials



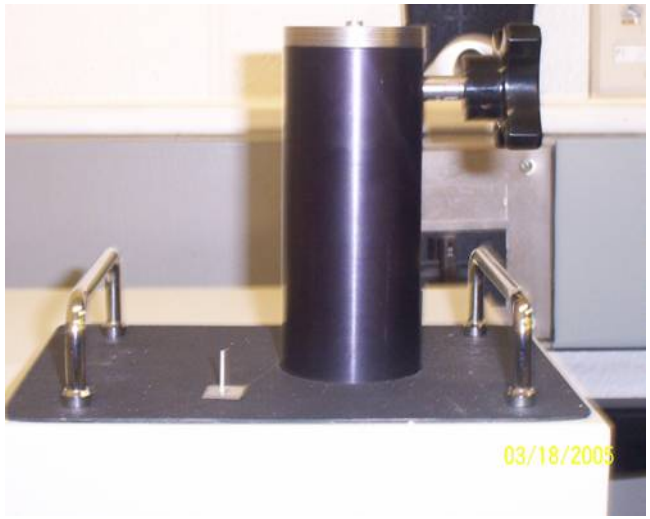




G#27/Anode interface after 11 cycles in Ar/H_2 atmosphere

From Ron Loehman, Sandia

Glass-metal adhesion strength measured by pin-pull test



Romulus adhesion testing machine- Quad Group Inc.

Sample	Failure Stress (MPa)	Notes
G#27/Crofer APU 22	39.5 ± 4.2	Glass failure
G#27/430SS	44.7 ± 1.9	Glass failure
G#36/Crofer APU 22	10.0 ± 0.8	Interface failure
G#36/430 SS	19.2 ± 0.7	Interface failure

Research Plans

Compositional development

- Crystallizing and non-crystallizing compositions
  - Viscosity and crystallization kinetics
- Design guidance for desirable properties

NEXTECH MATERIALS

Seal studies

- Glass-metal reaction chemistry
- Hermeticity and cell tests
  - Univ. Cincinnati
  - Univ. Connecticut
  - NexTech, et al.

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.
    - Vaporization
    - Interfacial reactions

Thank you for your attention!