

Sealing Materials for Solid Oxide Fuel Cells

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Outline

Goal: Develop stable, resilient sealing materials for SOFCs

- Reviewing the problem; initial glass development research
- Progress over the past six months
 - Glasses with greater CTE's
 - Developing composite materials
- Summarizing our program

The sealing problem is a challenge

1. Challenging compositional design problem

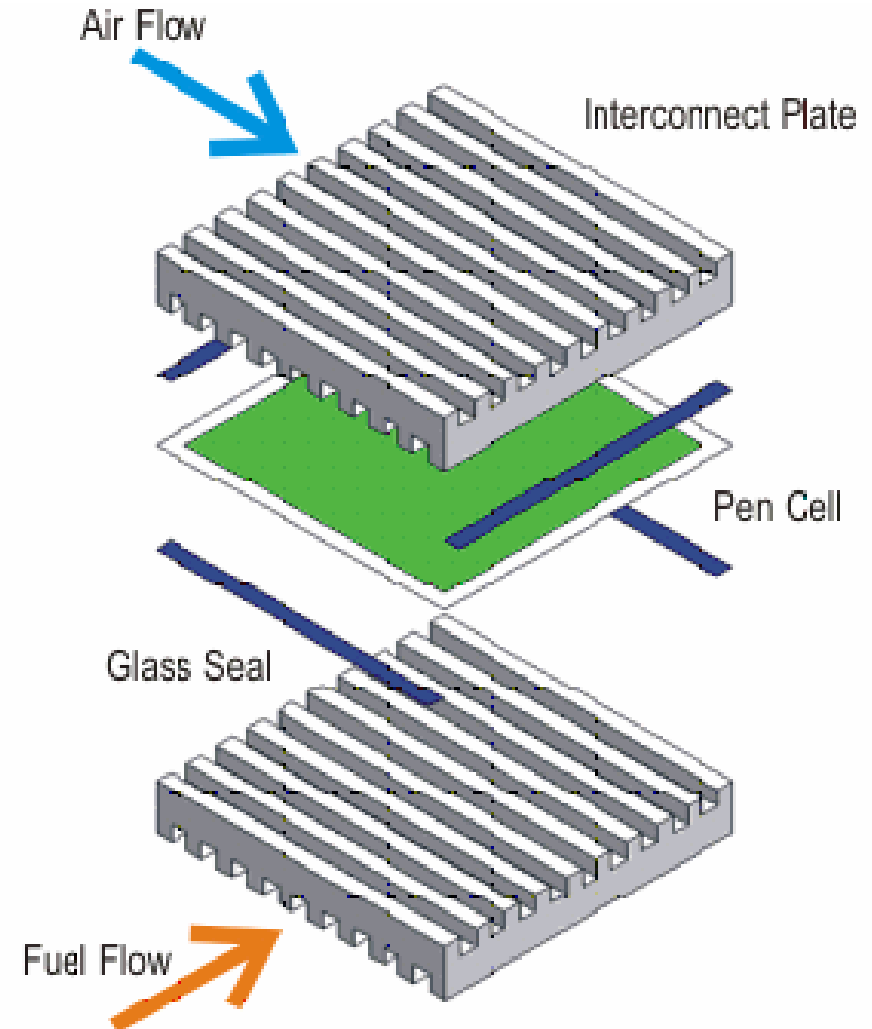
- Uncommon combination of properties
- Investigate uncommon families of glasses

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



Sealing glass properties depend on composition

Glass forming system under study:

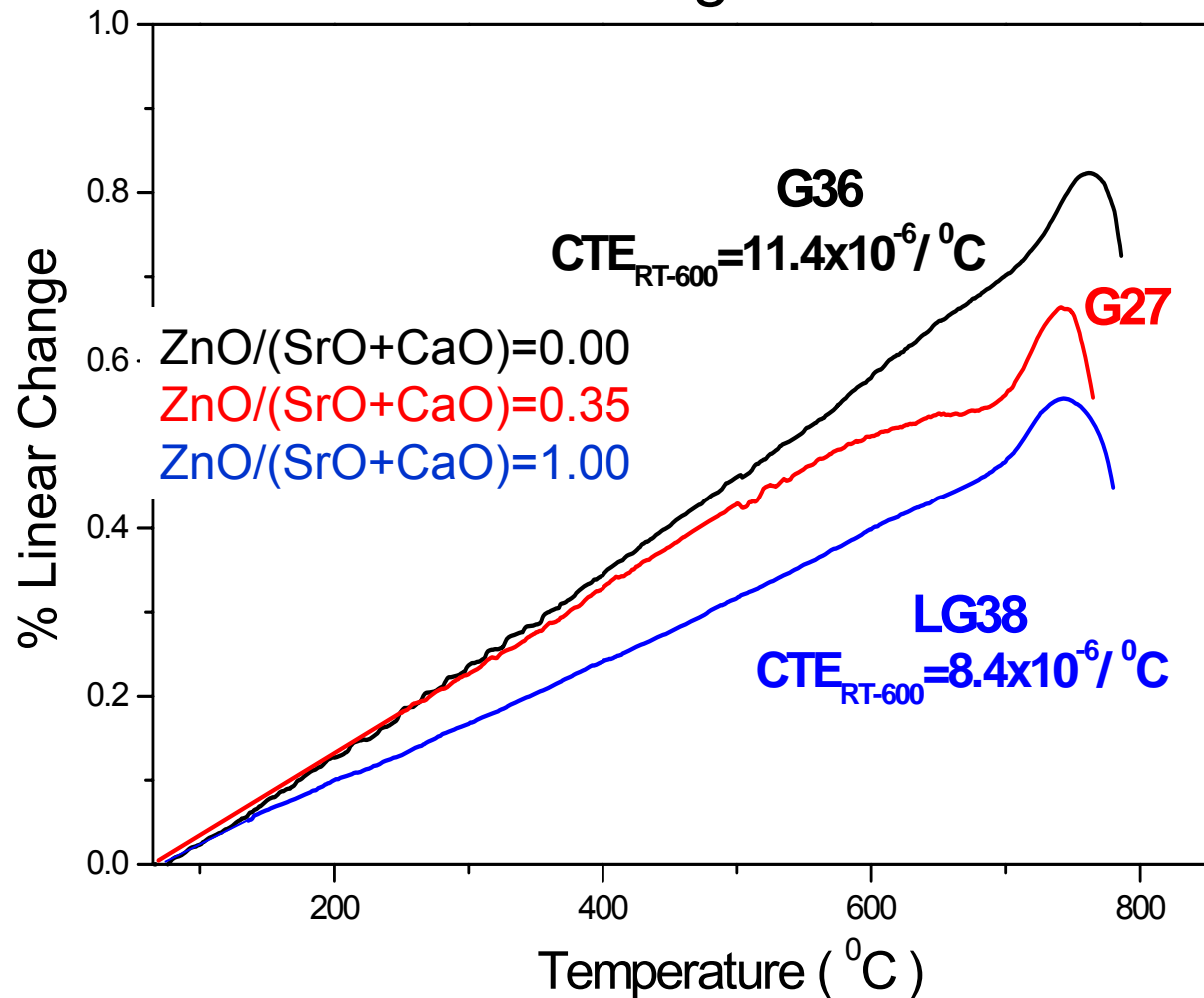
• Alkaline earth/zinc pyrosilicates

- 35-50 SiO₂
- 30-50 RO (R=Mg, Ca, Sr, Zn; no Ba)
- 0-10 B₂O₃, Al₂O₃, TiO₂, etc.

Design targets include:

- $10 < \text{CTE} < 13 \text{ ppm}/^\circ\text{C}$
- $800^\circ\text{C} < T_{\text{seal}} < 900^\circ\text{C}$
- Thermochemical and thermomechanical stability

"As made glasses"



Sealing glass properties depend on composition

"As sealed glasses"

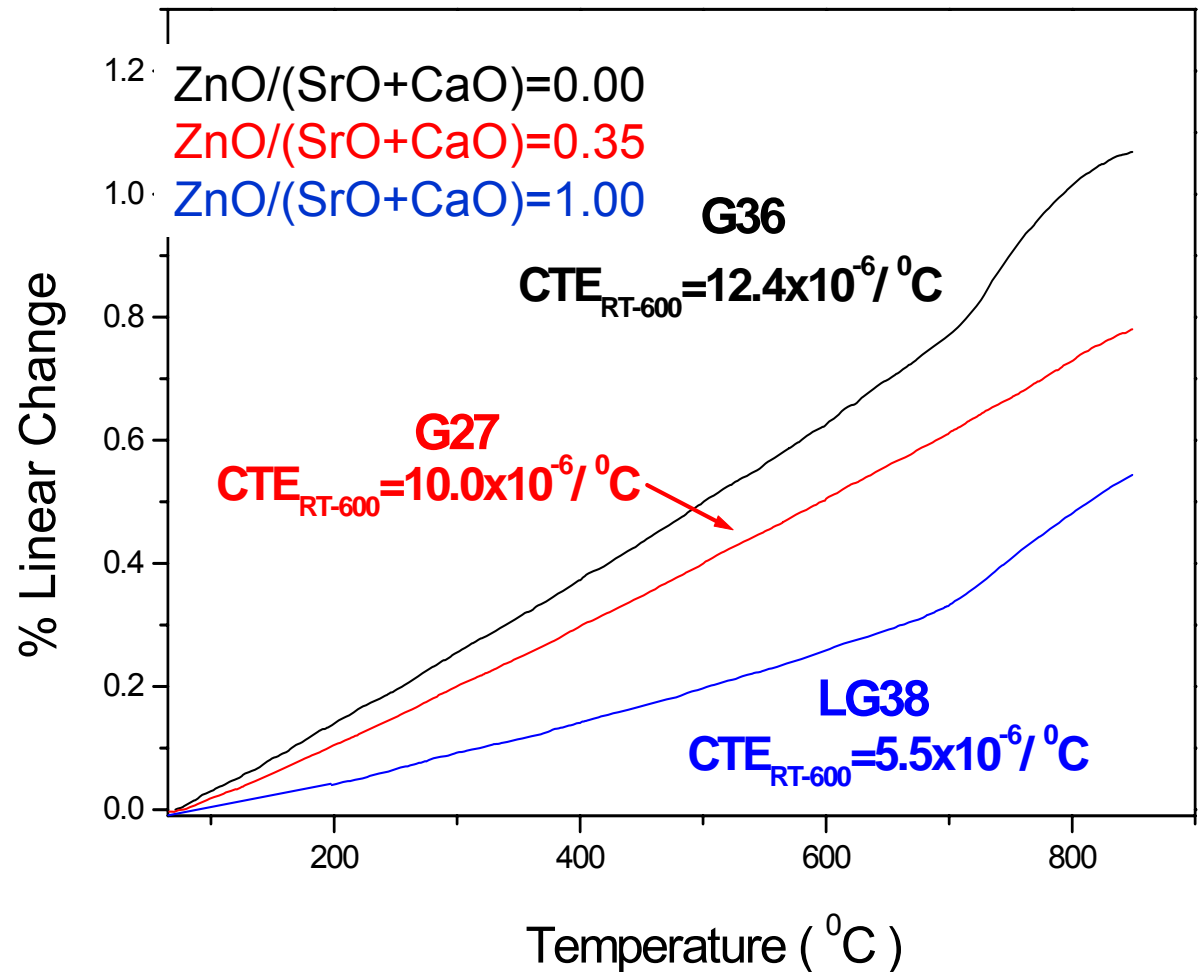
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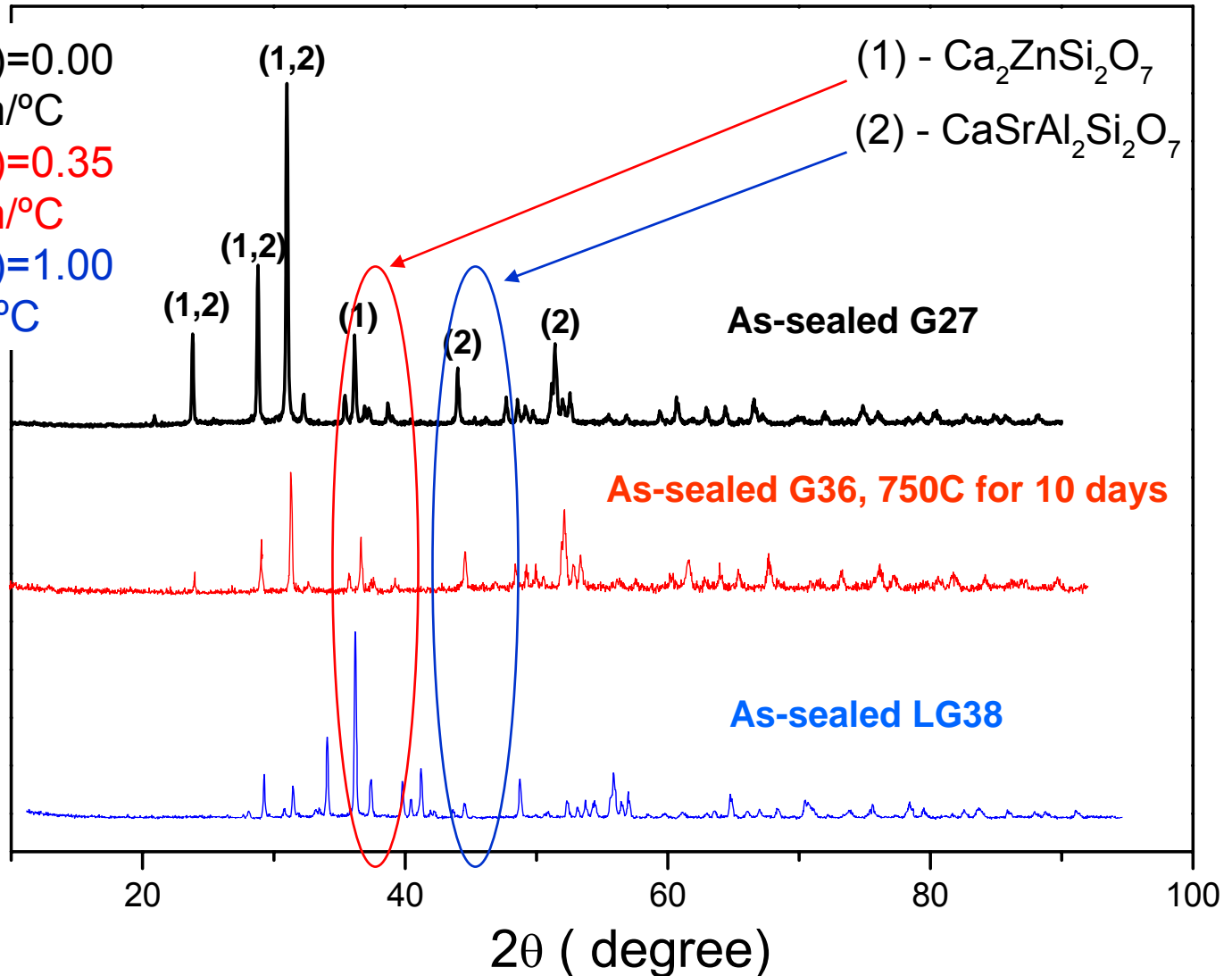
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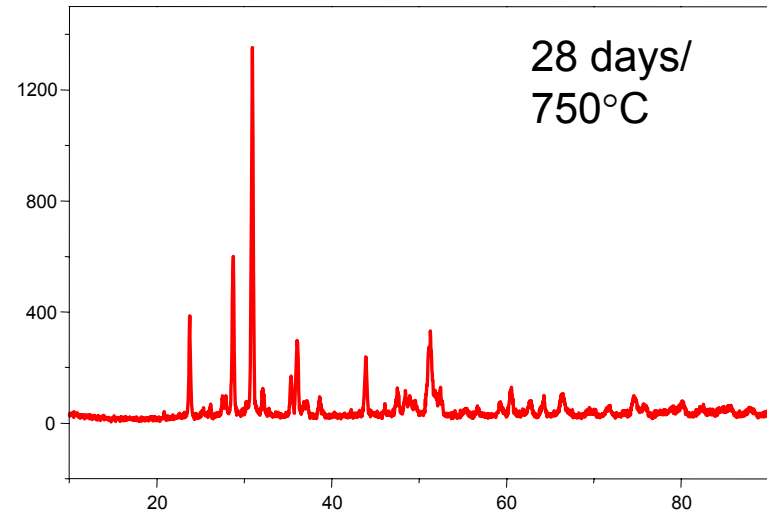
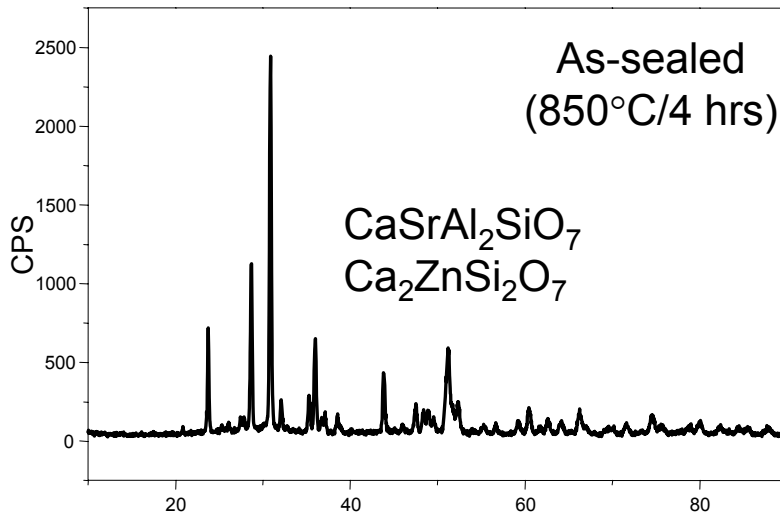
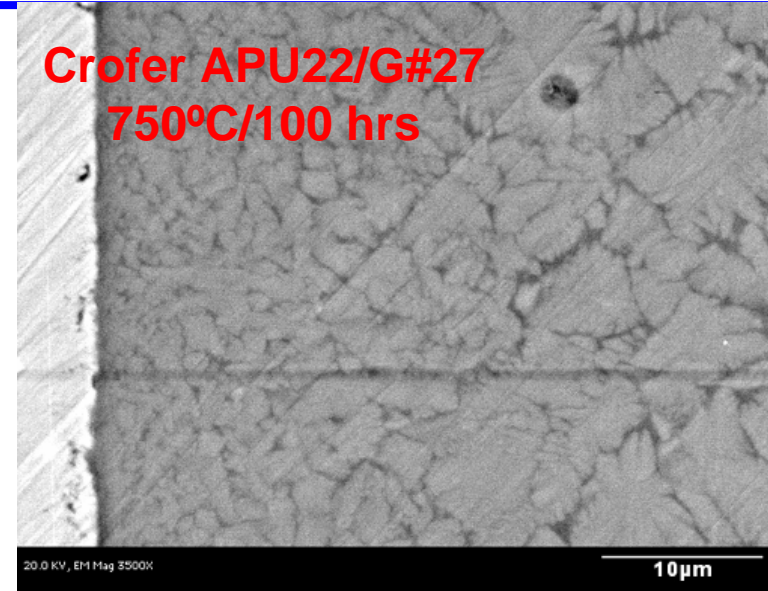
Thermal properties of sealing glasses are controlled by the ZnO/RO ratio

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

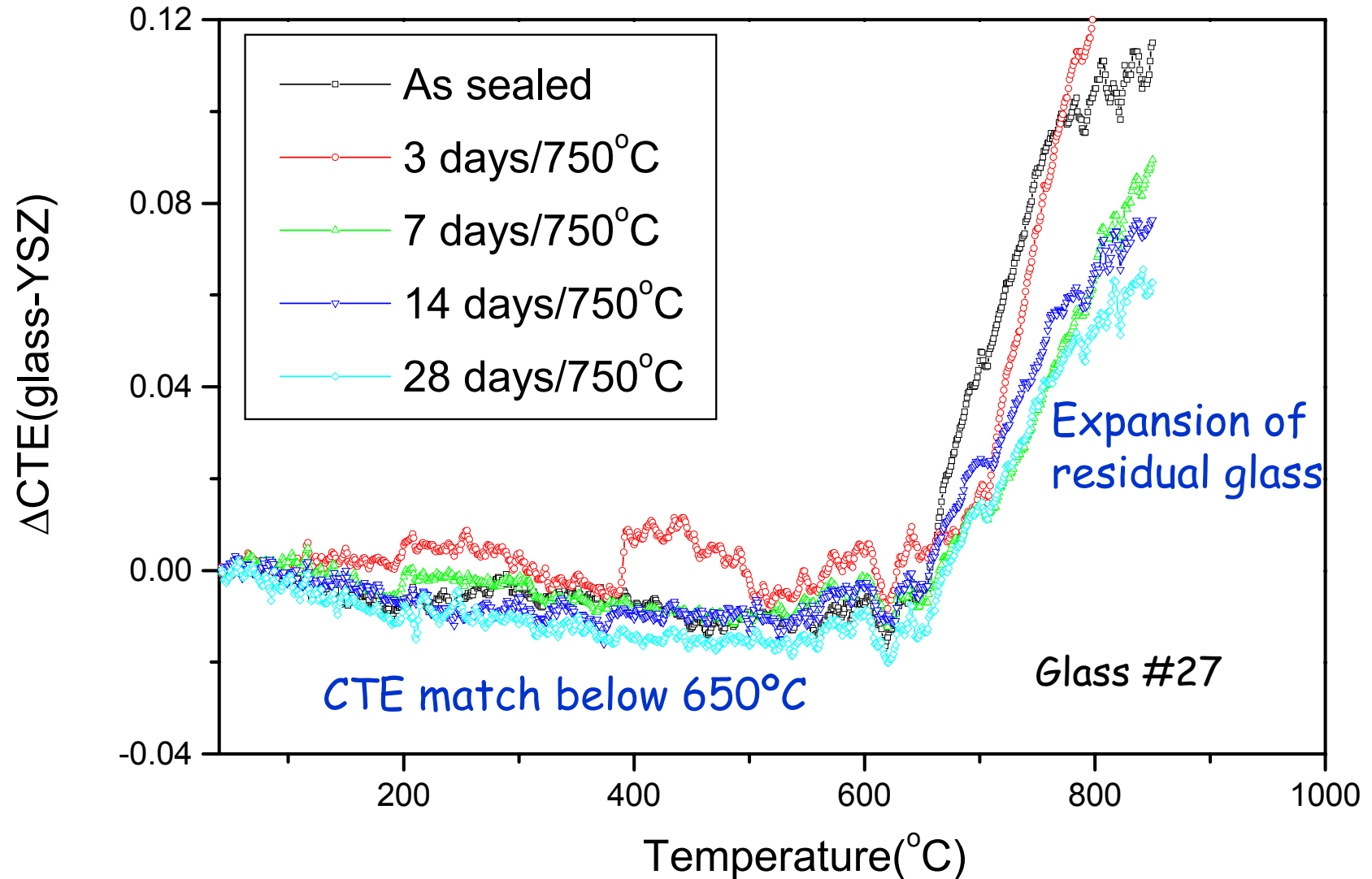


Representative crystalline phases in the UMR glass-ceramics

- **Pyrosilicates**
 - $\text{CaSrAl}_2\text{SiO}_7$, $\text{Ca}_2\text{ZnSi}_2\text{O}_7$
- **Orthosilicates**
 - Sr_2SiO_4 , Zn_2SiO_4
- Composition is most important parameter for final phase distribution.



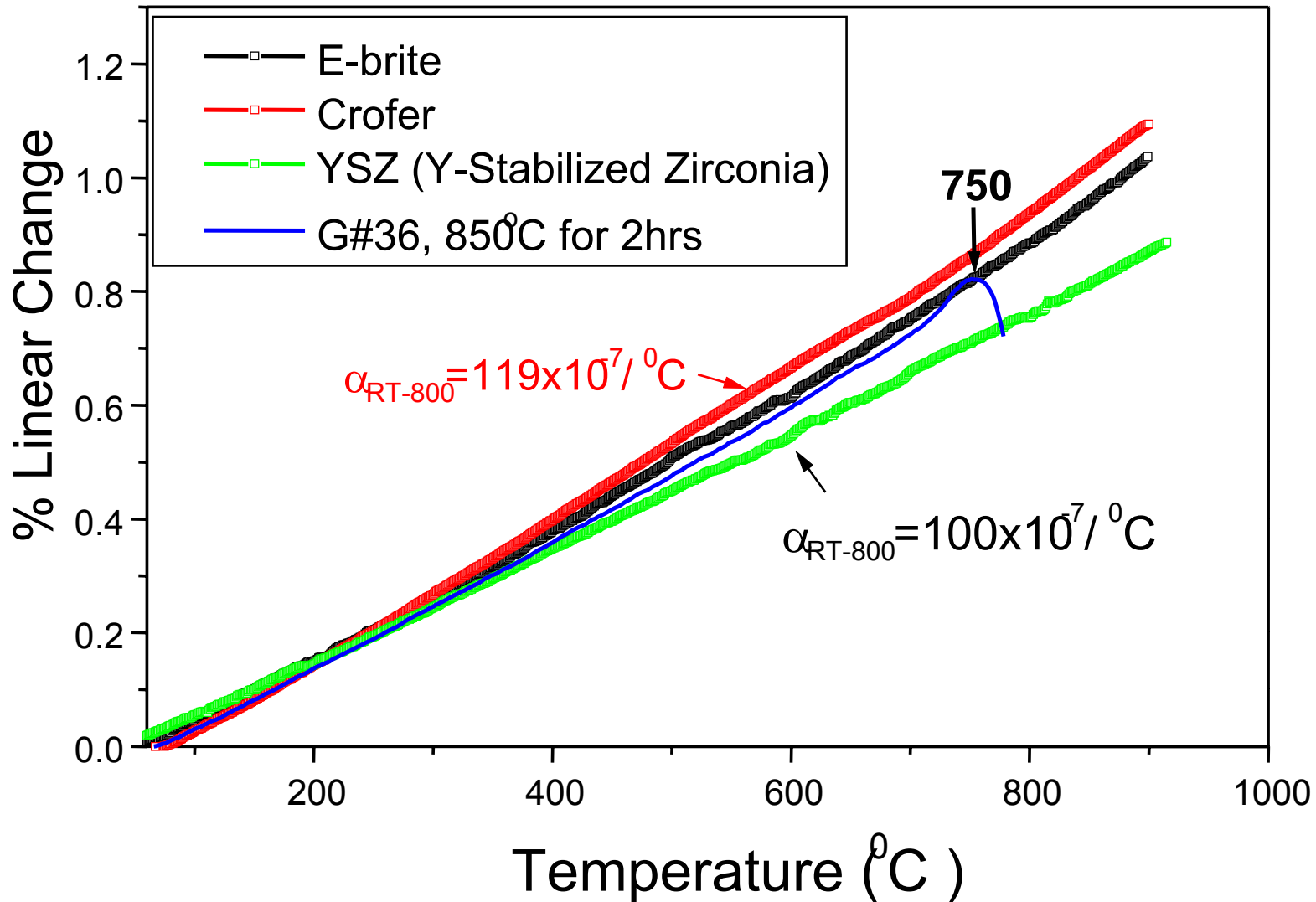
Glass#27 possesses a good CTE-match with YSZ



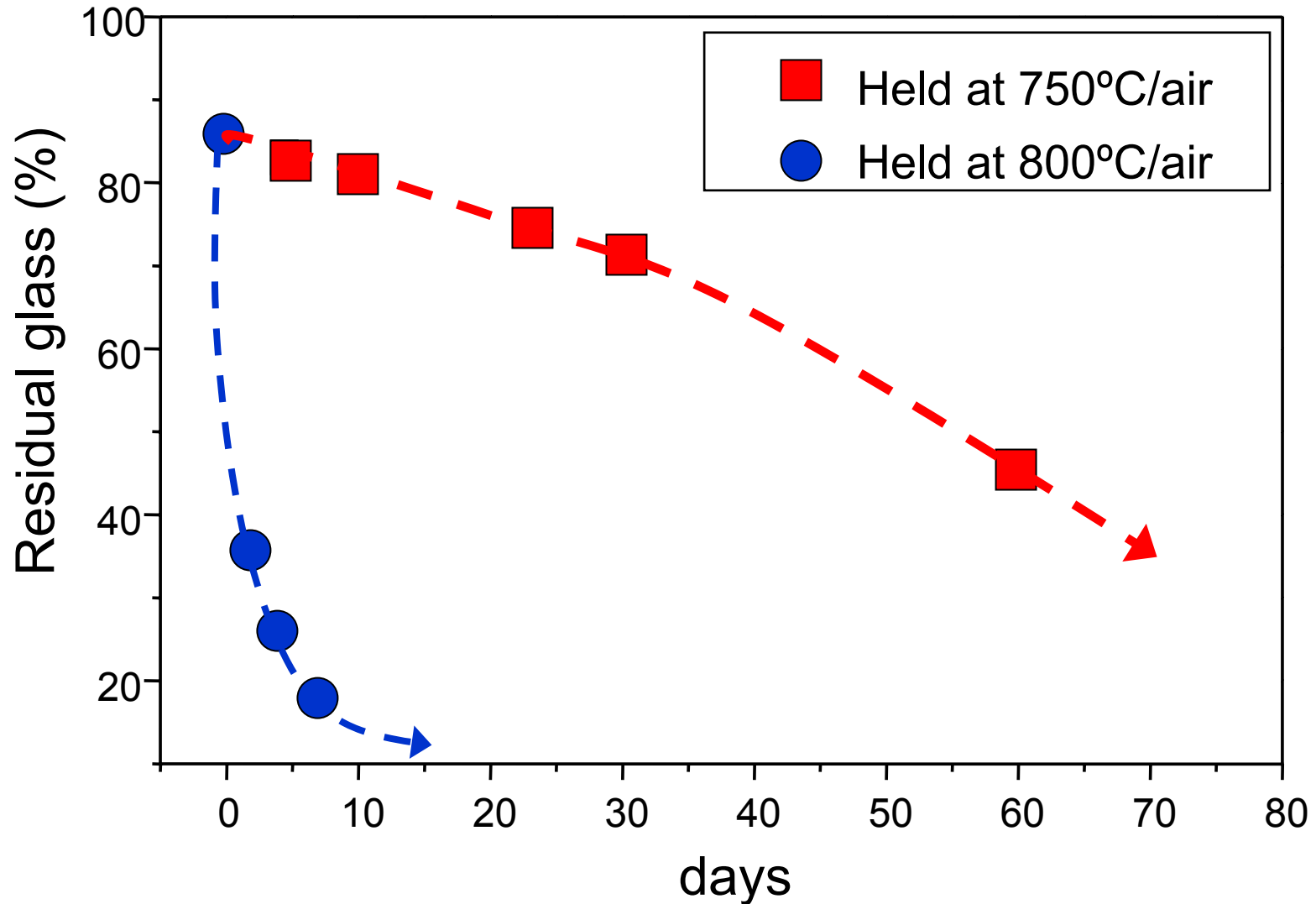
Greater CTE's are needed for some SOFC designs

- Compositional modifications include
 - Replacing ZnO with CaO and SrO
 - Reducing Al₂O₃ content
 - Modifying relative SiO₂ and B₂O₃ contents
- About fifteen new compositions prepared this past reporting period

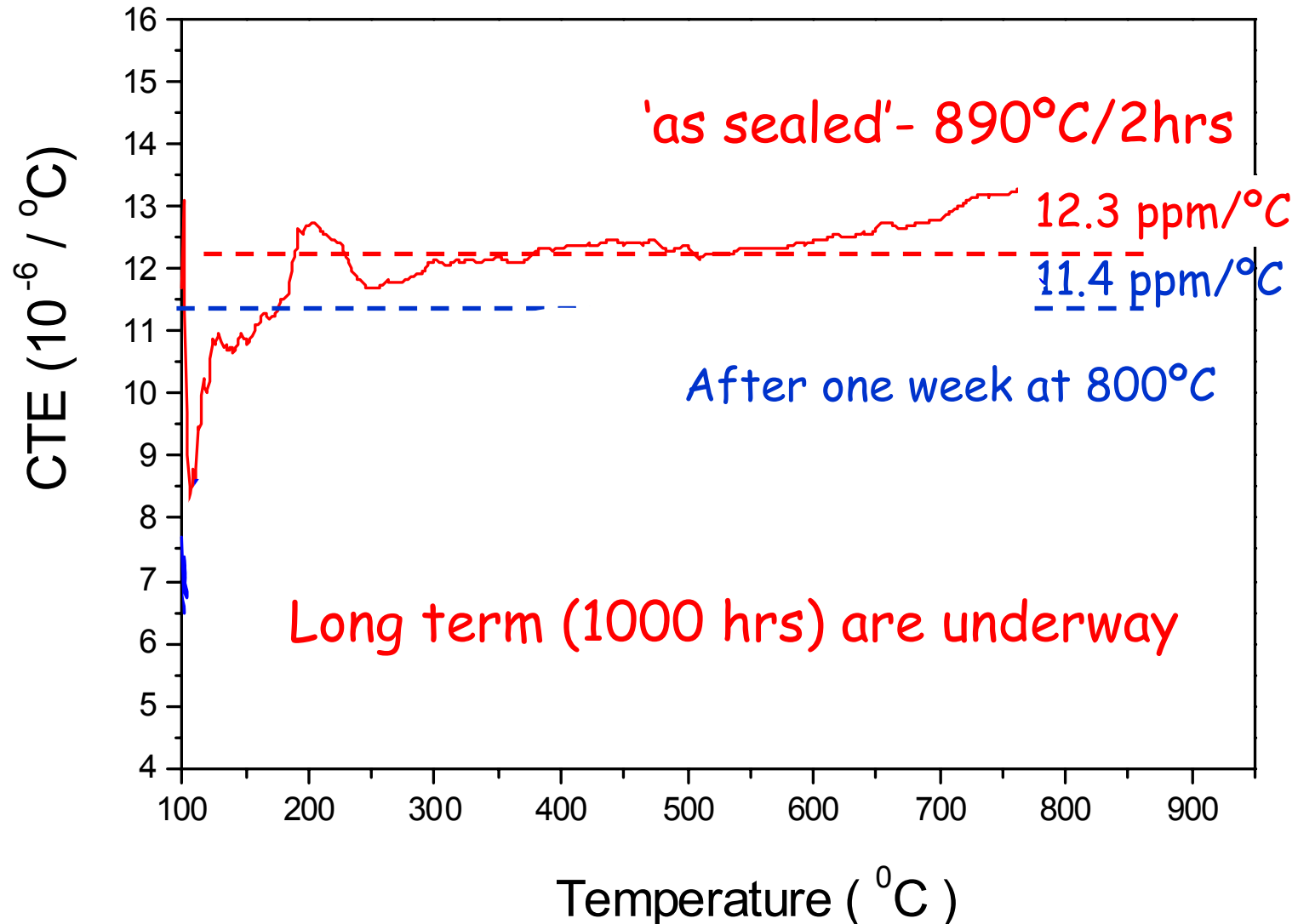
Glass #36 may be more appropriate for some SOFC designs



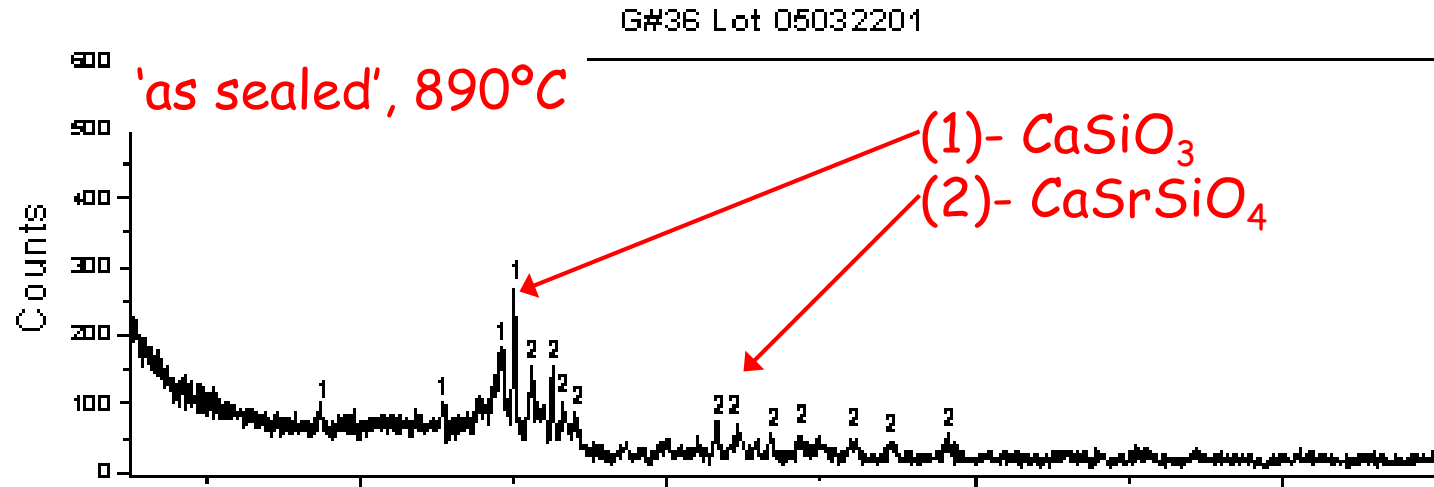
Crystallization Kinetics of Glass#36/DTA Analyses



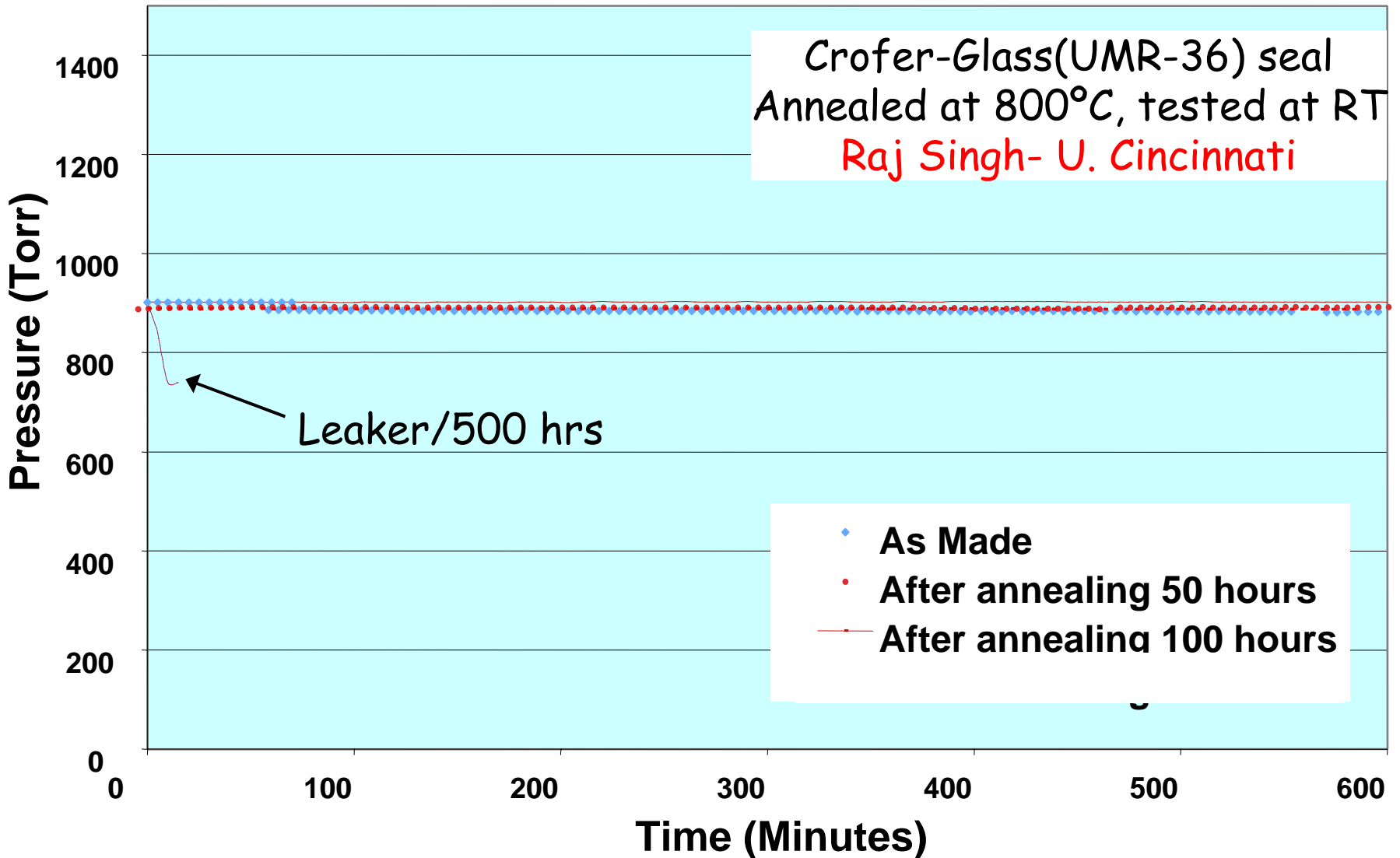
The CTE of glass#36 changes at 800°C



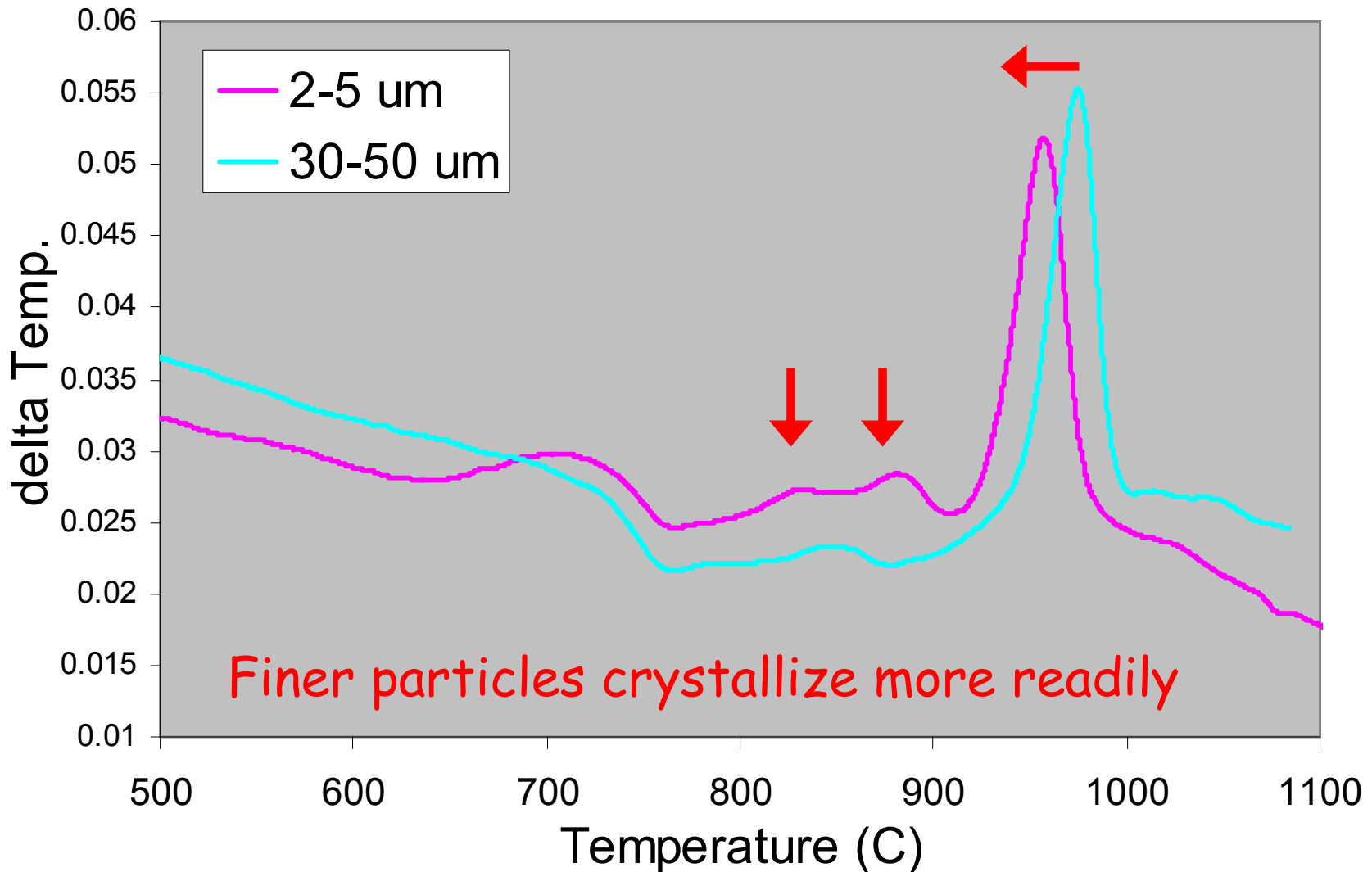
Ca-silicate phases form on crystallization



Initial Hermeticity Tests- Mixed Results

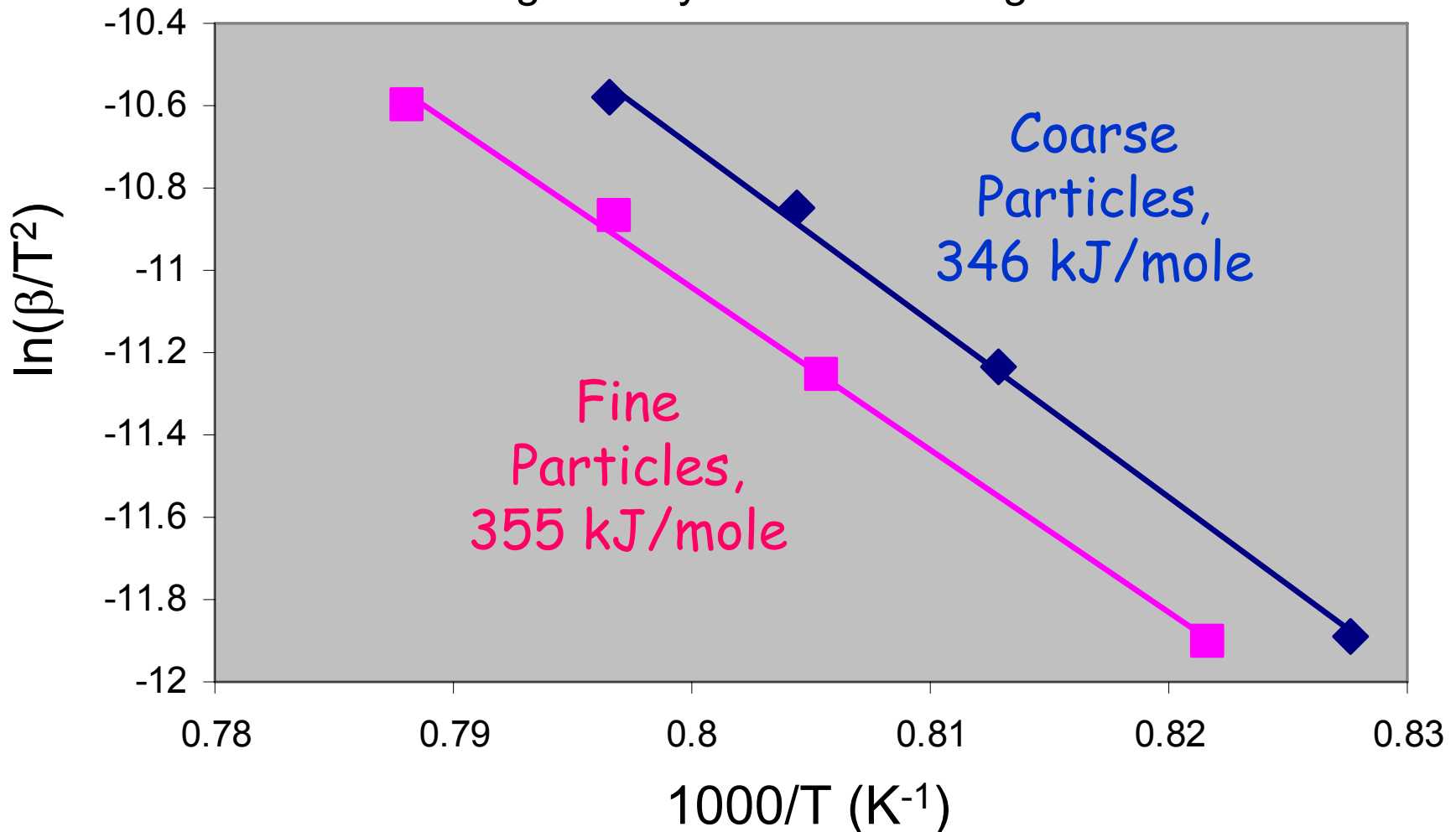


We use DTA to characterize processing effects on properties

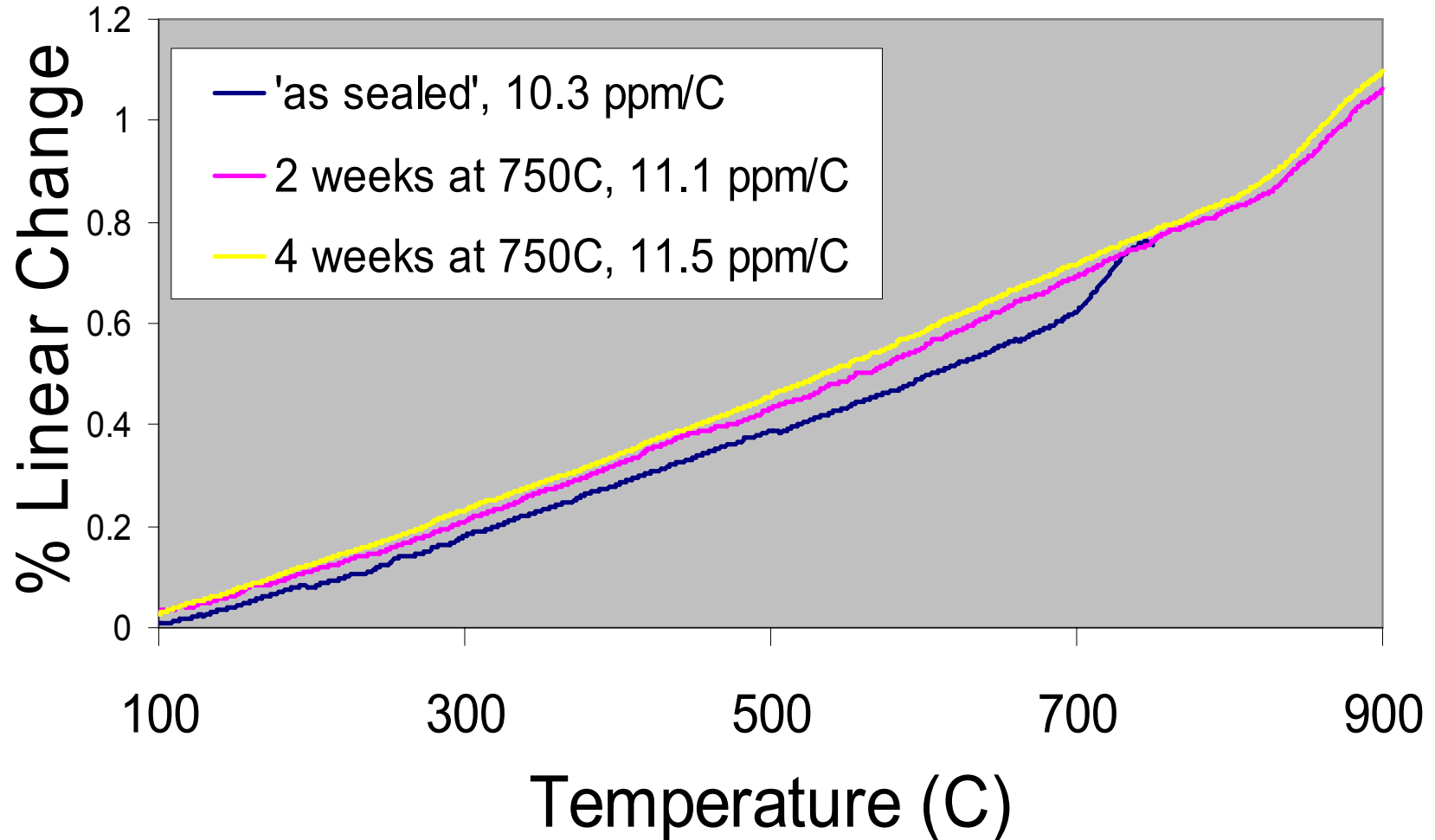


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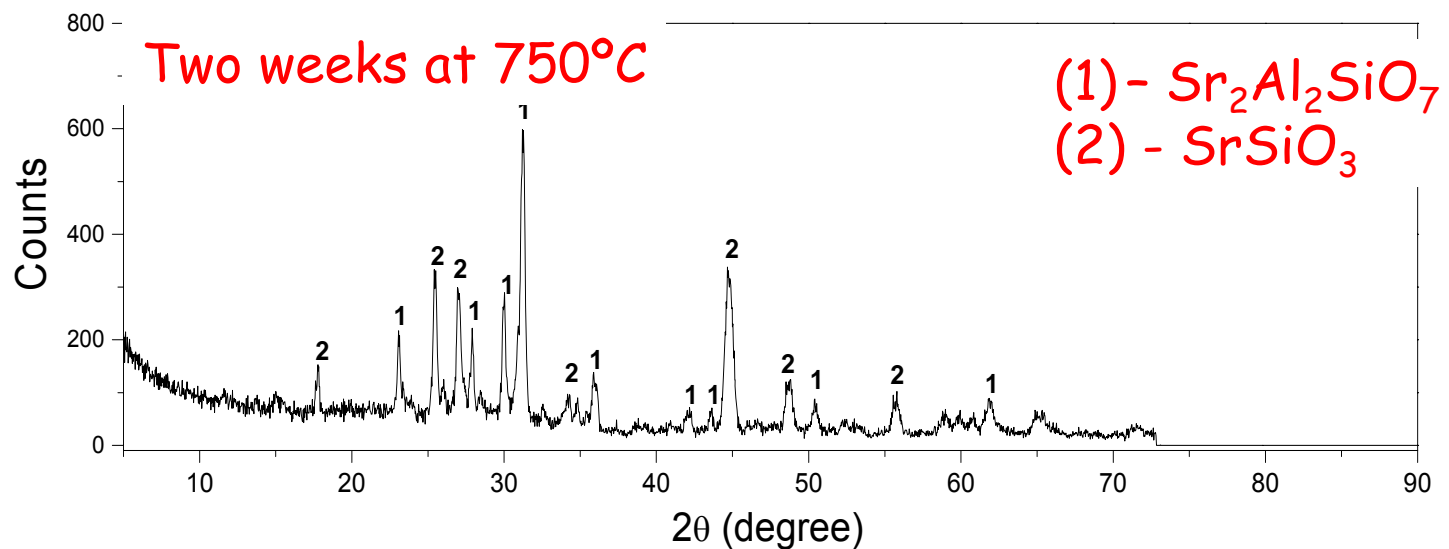
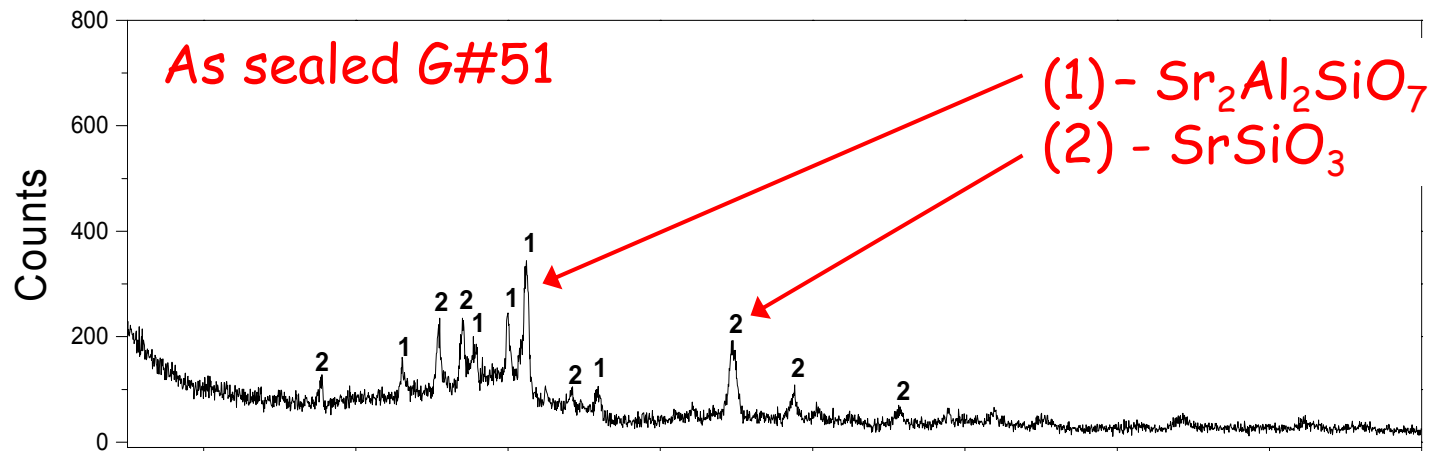
Kissinger analysis: DTA heating rates



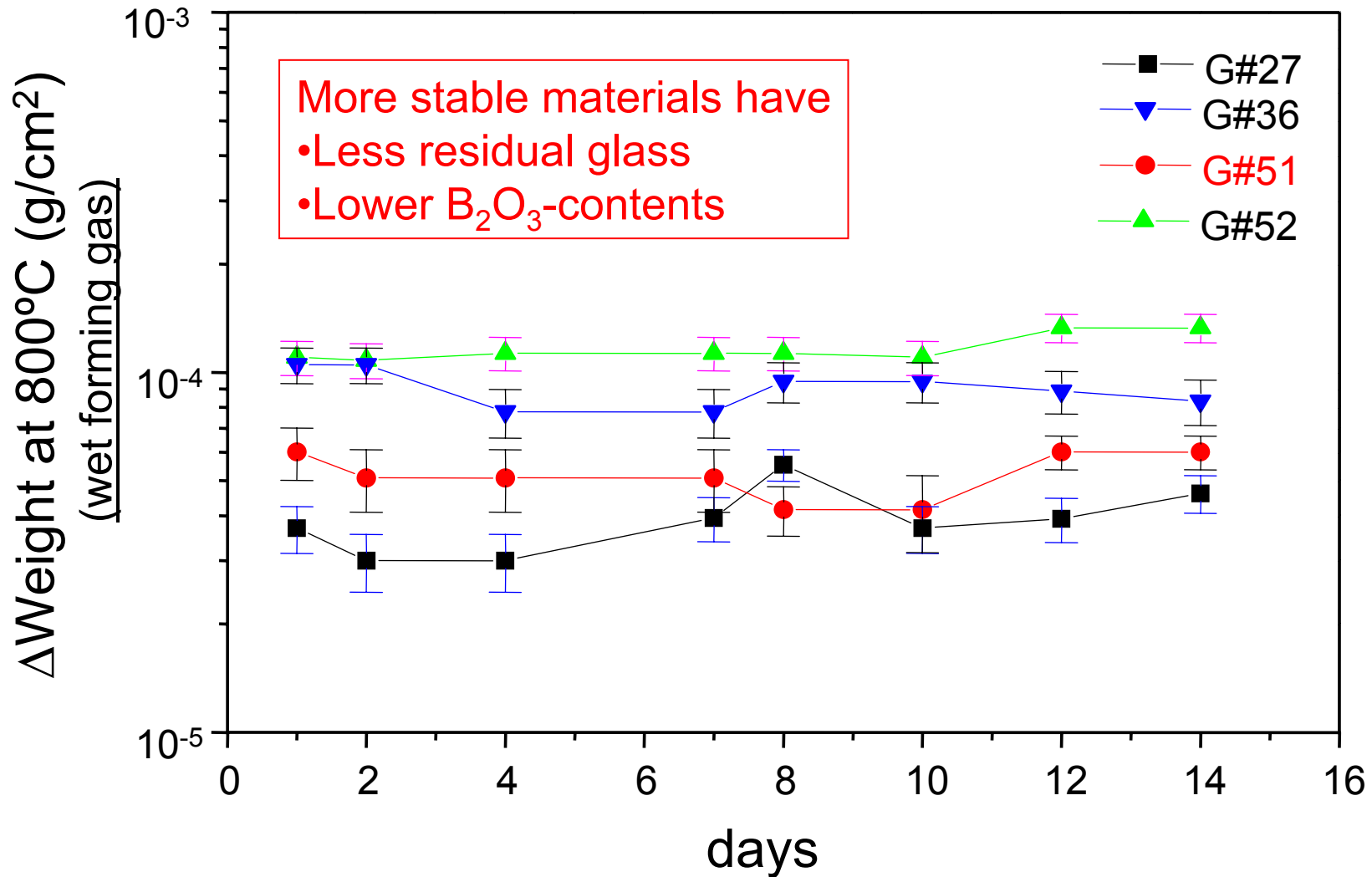
Glass#51 has promising dilatometric characteristics



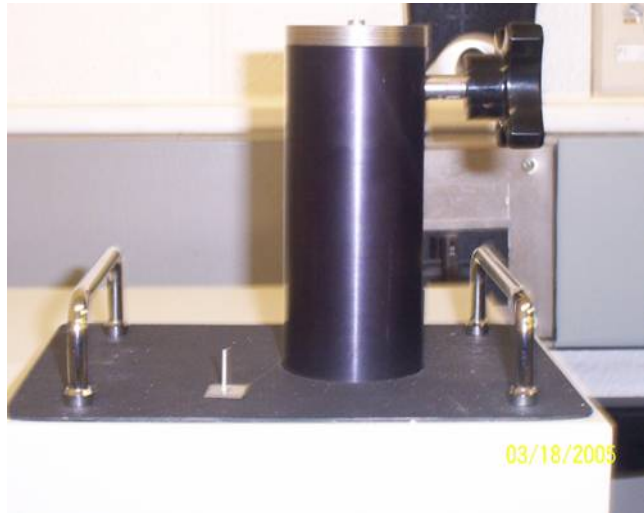
Sr-silicate phases form on crystallization



Glass stability in wet forming gas (800°C)



Glass-metal adhesion strength measured by pin-pull test



Romulus adhesion testing machine- Quad Group Inc.

~300 μ m glass coatings on interconnect substrates; 'as sealed' and after heat treatments



G51/430SS- 'as sealed'	20.9 \pm 6.9 MPa
G51/430SS- 750°C/700hrs	20.7 \pm 10.2 MPa
G52/430SS- 'as sealed'	19.8 \pm 3.8 MPa
G52/430SS- 750°C/700hrs	18.9 \pm 2.6 MPa

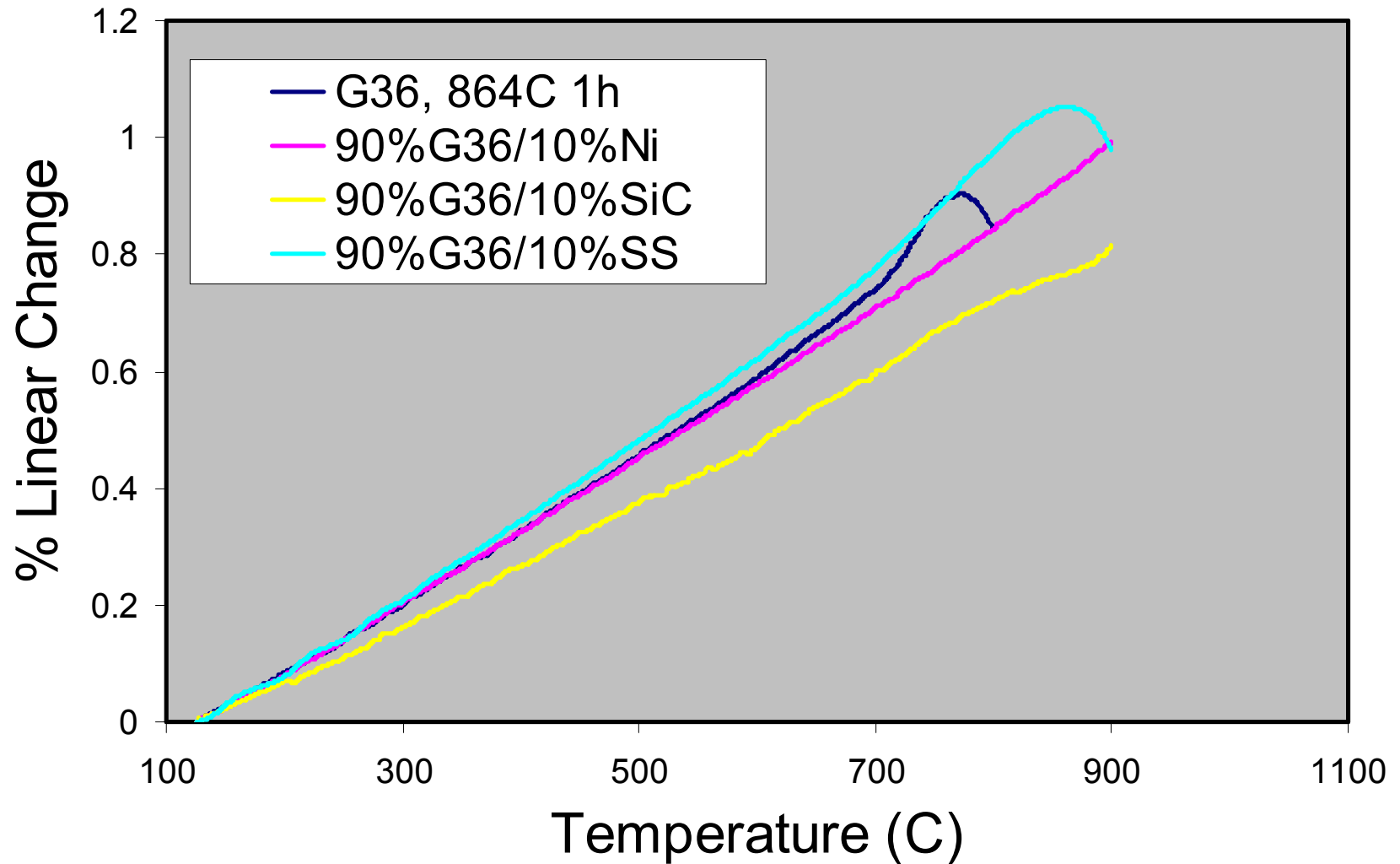
Sealing materials can be modified by adding fillers

- Tailor CTE
- Control crystallization
- Affect interfacial reactions
- Relieve thermal stresses
 - Controlled cracking in glass matrix; healing by viscous flow of residual glass
 - Design CTE and elastic mismatches

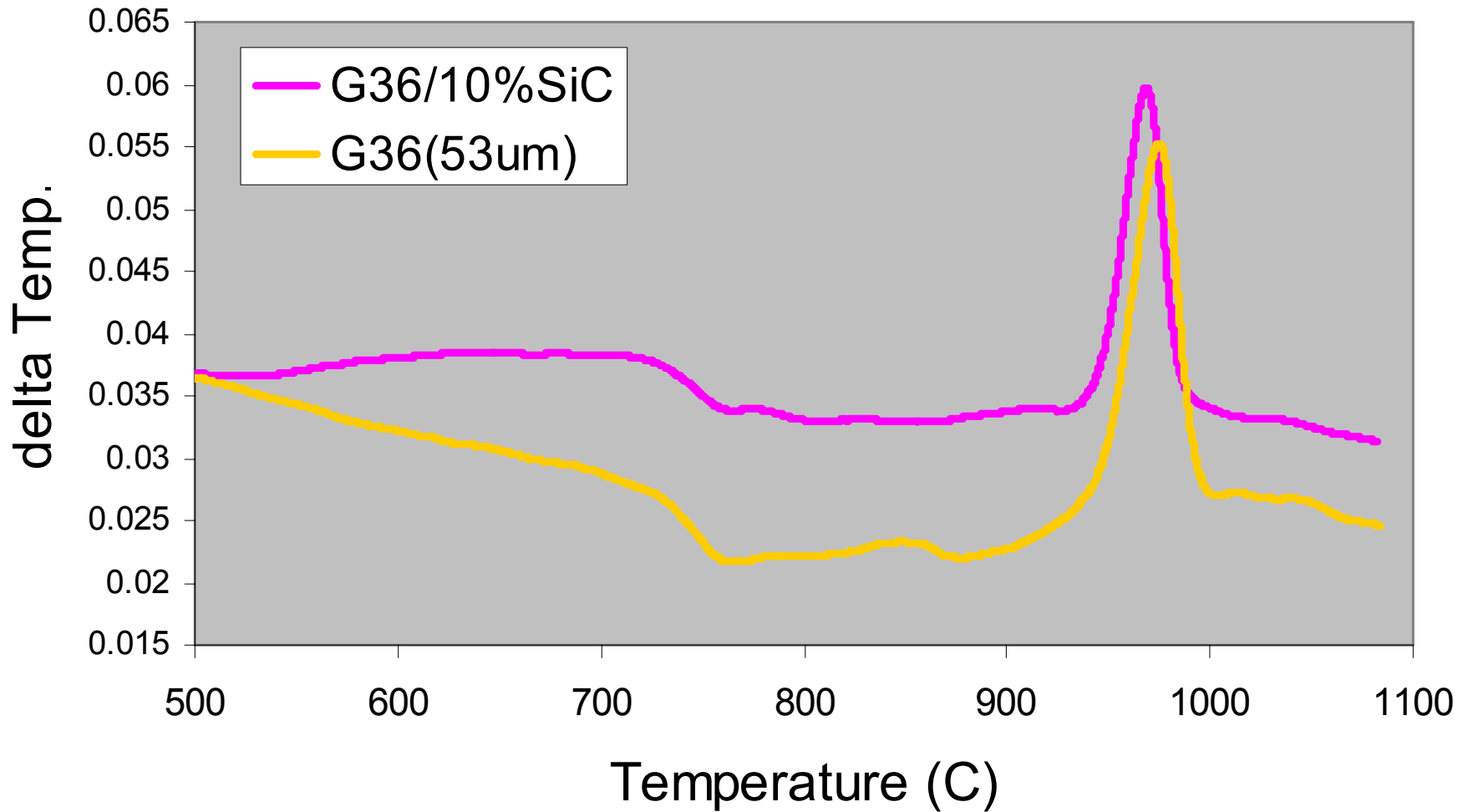
Composite Overview

Material	CTE (ppm/°C)	Elastic Modulus (GPa)	Notes
G36	12.1	80	
Ni	13.3	207	
Mo	5.1	324	
316SS	17	193	
Ti-Ni		34-83	Phase transition
WC	5.2	669	
SiC	4.3	483	
Quartz	7.0→13.3		Phase transition
ZrO ₂	7.0→10.5	138-210	Phase transition

Dilatometric characteristics depend on filler



Composite crystallization behavior will be characterized by DTA



Experiments Underway

- Composite processing
 - Dense seals using tape-casting techniques
- Composite properties
 - Tailoring CTE
 - Induced cracking?
- Composite reactivity
 - Filler/matrix compatibility'
 - SOFC interfaces

SOFC Seal Summary

- SOFC seals offer an interesting materials challenge
- RO- polysilicate compositions have promising combinations of properties
 - Polysilicate 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.
- Composite seals based on RO-polysilicate glasses
 - Reduce stresses due to thermal cycling?

Thank you for your attention!