Frits and Sealing

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Presented at Lehigh University as part of
IMI-NFG Series on Glass Processing

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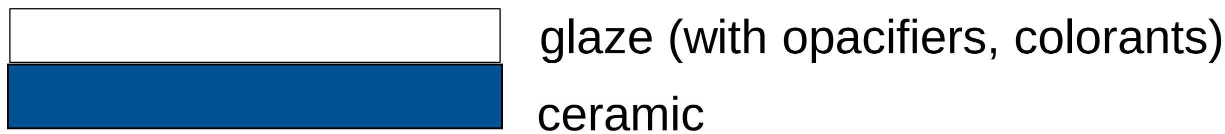
Lectures available at:
www.lehigh.edu/imi

Powdered glasses (frits)

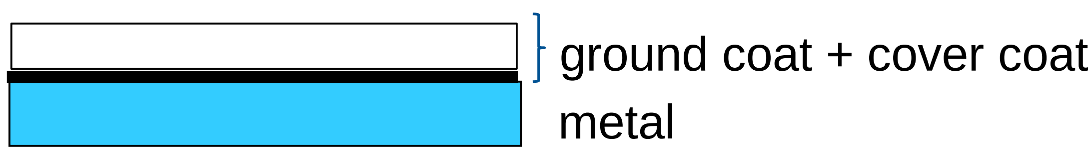
- Sealing Frits –

- Coatings

  glazes –

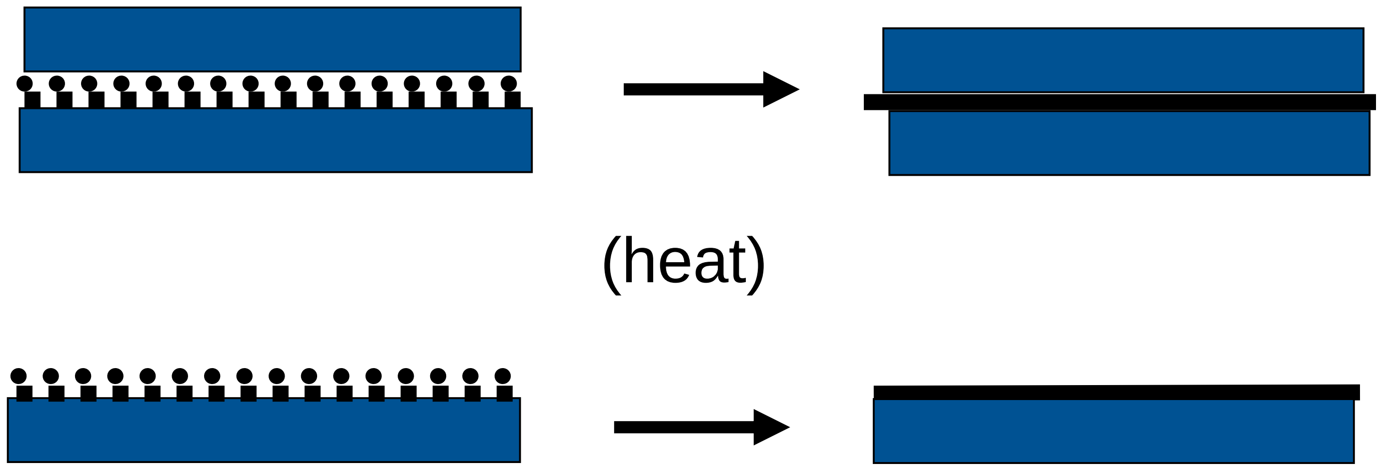


  porcelain enamel -



Starting point

- Frits – finely powdered glasses that when re-heated will sinter, soften, and flow to form a seal or a coating



At start:
unconsolidated frit powder

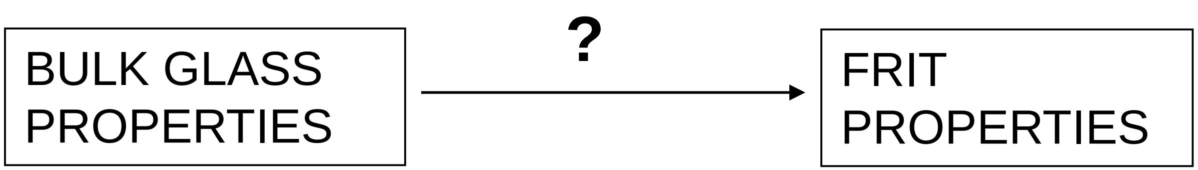
At finish:
strong, hermetic seal
or impervious coating

Overview

- Brief introduction, frits vs bulk glasses
- Selection criteria for design of frit composition
- Processing of frits

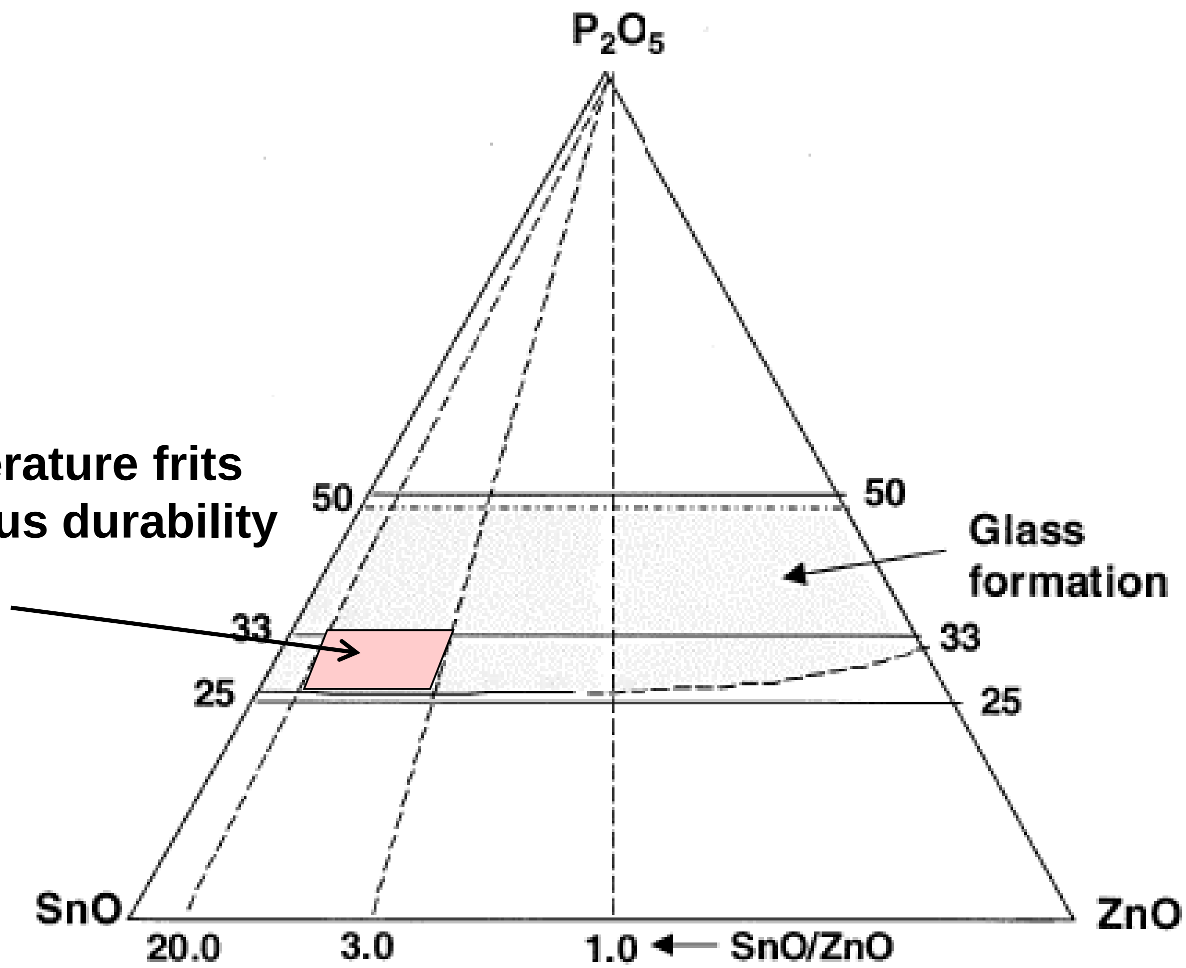
Bulk glass vs frit behavior

- By definition, glass is a thermodynamically unstable structure.
- Converting a bulk glass to a fine powder only increases its instability.
- Relatively few bulk glasses are stable as frits, but will crystallize to at least some extent



SnO-ZnO-P_2O_5 system

Stable low temperature frits with good aqueous durability



Classifications of frits

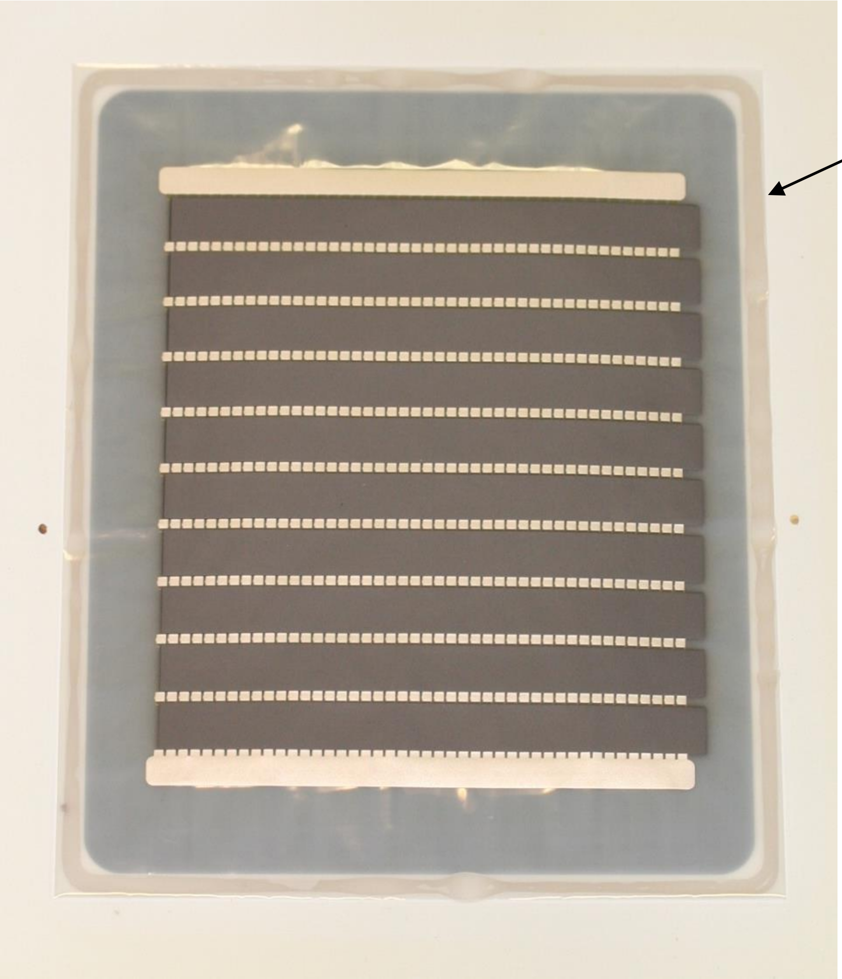
- **Vitreous** – remains glassy throughout sealing cycle; will soften and flow if re-heated
- **Devitrifying** – initially glassy, but at some point during sealing cycle will crystallize to form a hard, rigid bond. If reheated, will not flow and soften.

- Typically, vitreous frits are desired where seals are subjected to repeat thermal cycling; devitrifying frits are preferred for applications in which the seal will be exposed to high operating temperatures

Selection criteria for design of frit composition

- Maximum permissible sealing temperature
- CTE of materials to be bonded (CTE compatibility)
- Use temperature of sealed assembly
- Other – durability, strength, hermeticity, required lifetime, IR absorbance

Frit-sealing:
SOFC (solid oxide fuel cells)

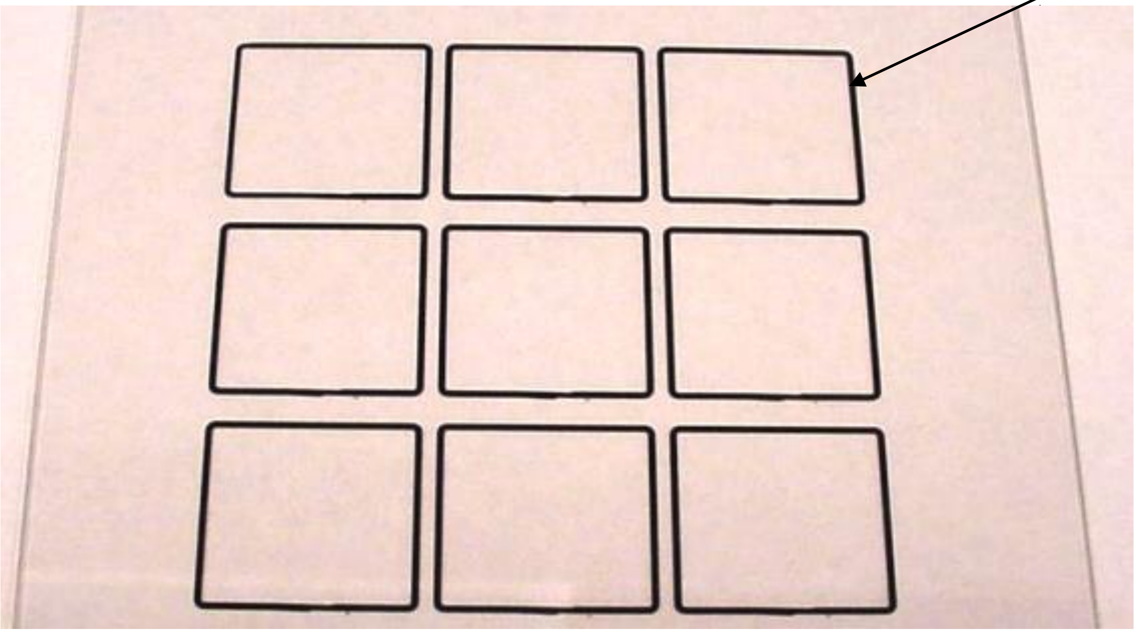


Frit seal

Requirements:

Max. sealing temp: 900°
CTE: 110-120
Service temp: 750º
Other: alkali-free, hermetic during extended (10Y) service time in H_2 environment.

Frit-sealing: OLED devices

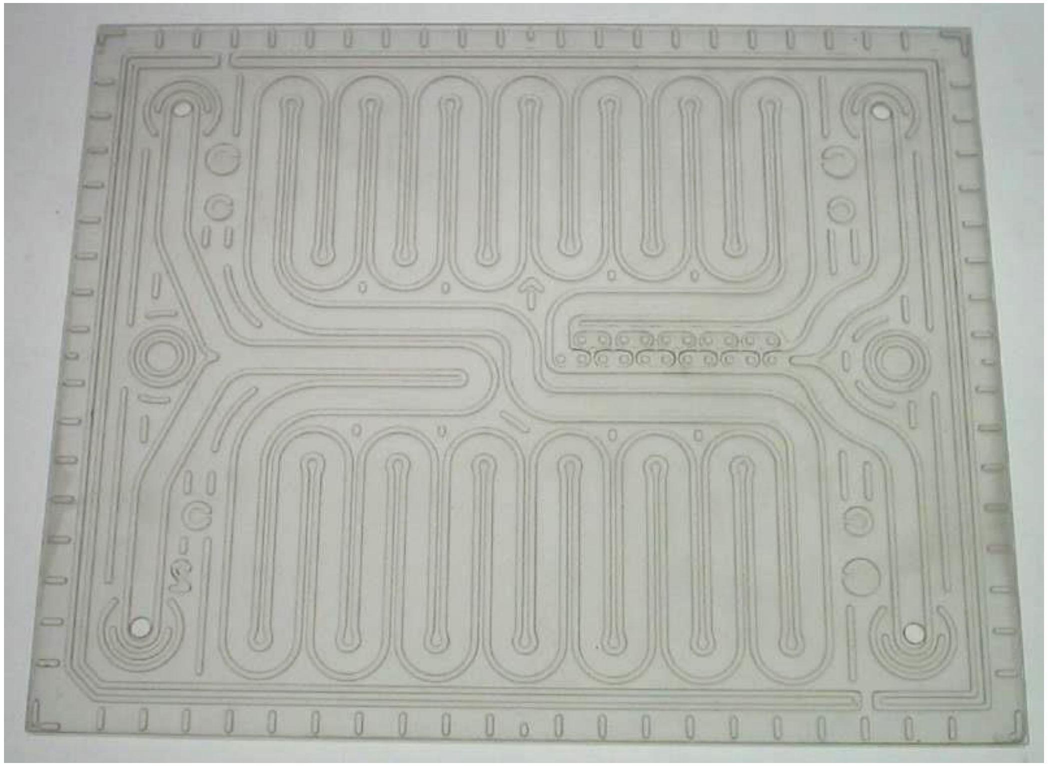


Frit seal

Requirements:

- **Max. sealing temp**: 450°
- **CTE:** 30-35
- **Service temp**: RT
- **Other:** hermetic during 5Y lifetime; laser-sealable since temp during sealing must be <100º 1mm from seal edge

Frit-sealing: Micro-reactors for chemical synthesis



Micro-reactors

Requirements:

- **Max. sealing temp:** 800°
- **CTE**: 35-40
- **Service temp:** -50º to +50º
- **Other:** high chemical durability (acids and bases)

Sealing temperature

For a frit, flow is everything – main determinant of sealing temperature

Straight $>10^9$ **P**

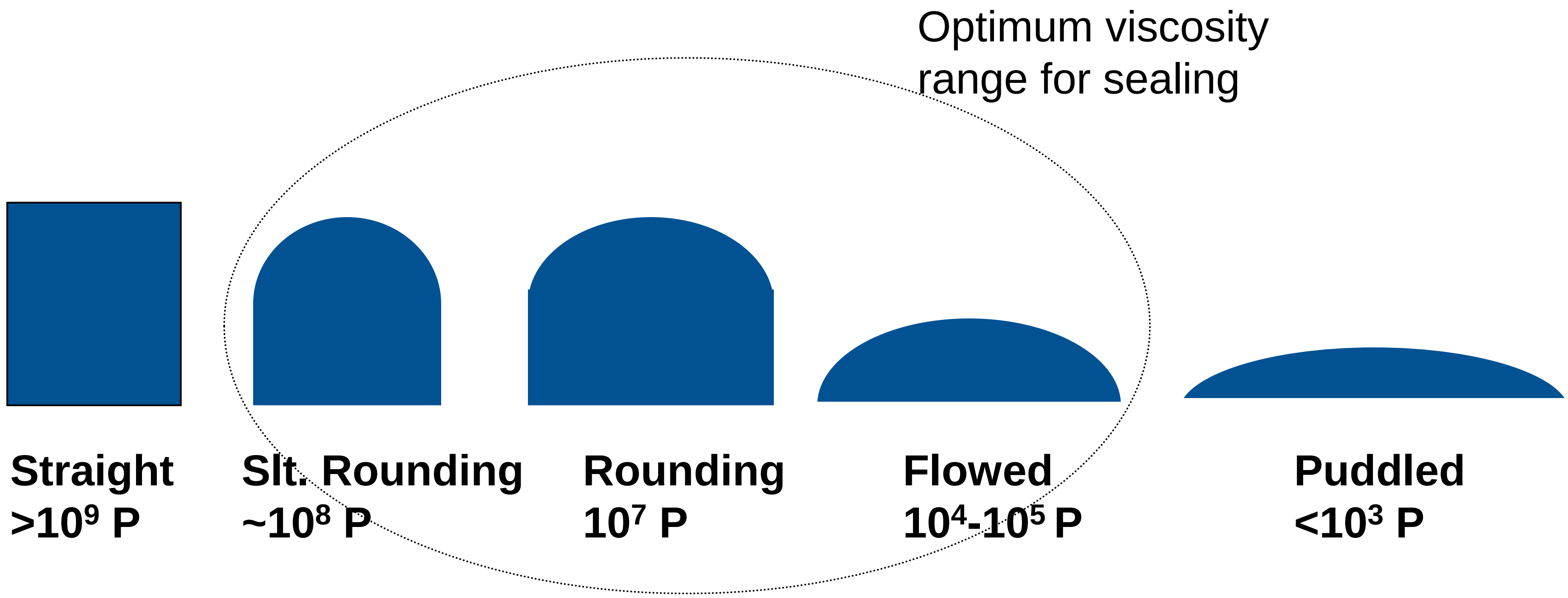
Slt. Rounding $\sim10^8$ **P**

Rounding 10^7 **P**

Flowed 10^4-10^5 **P**

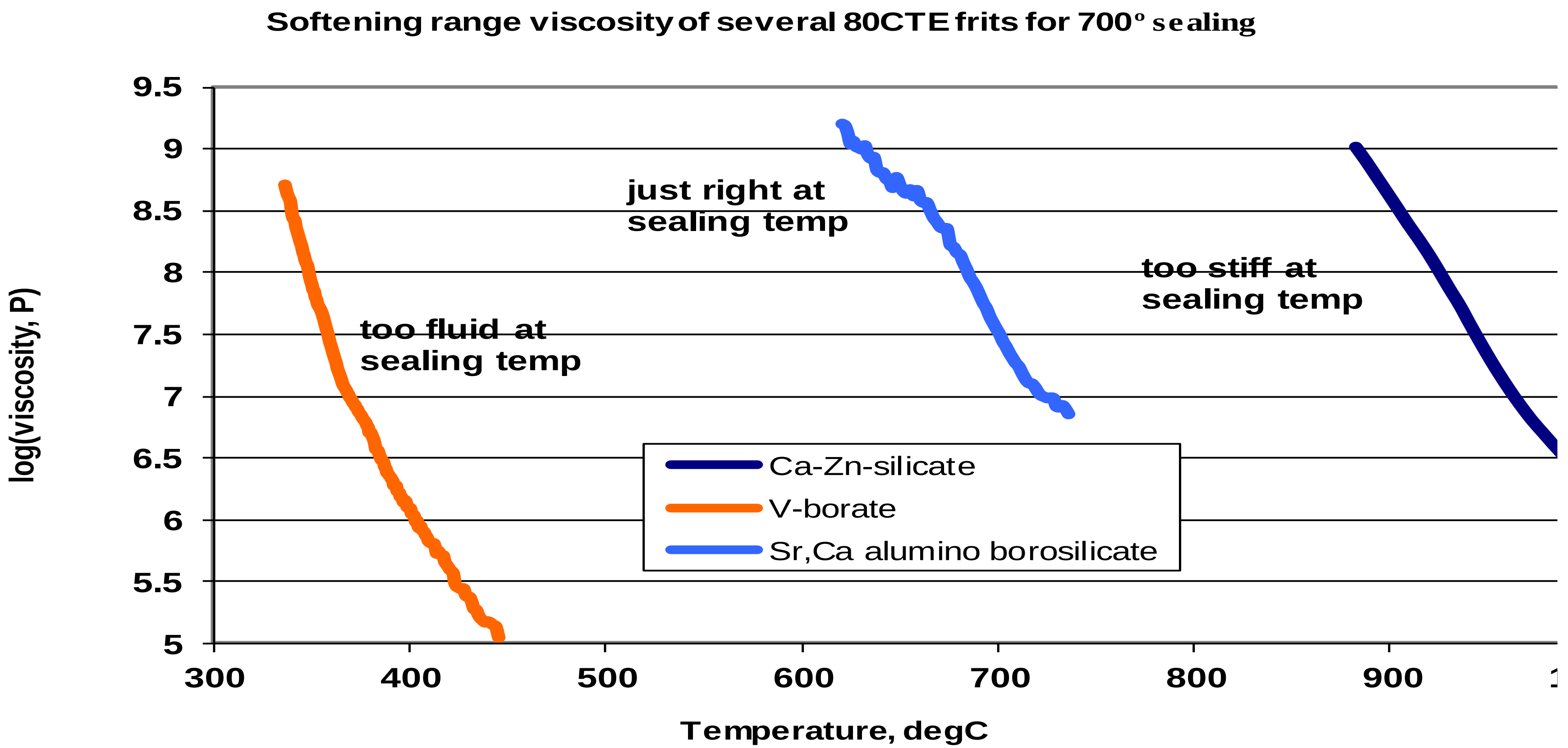
Puddled $<10^3$ **P**

For a frit, flow is everything



Selection criterion: Flow

- For strongest seal, seal temperature should correspond to the softening range of the frit

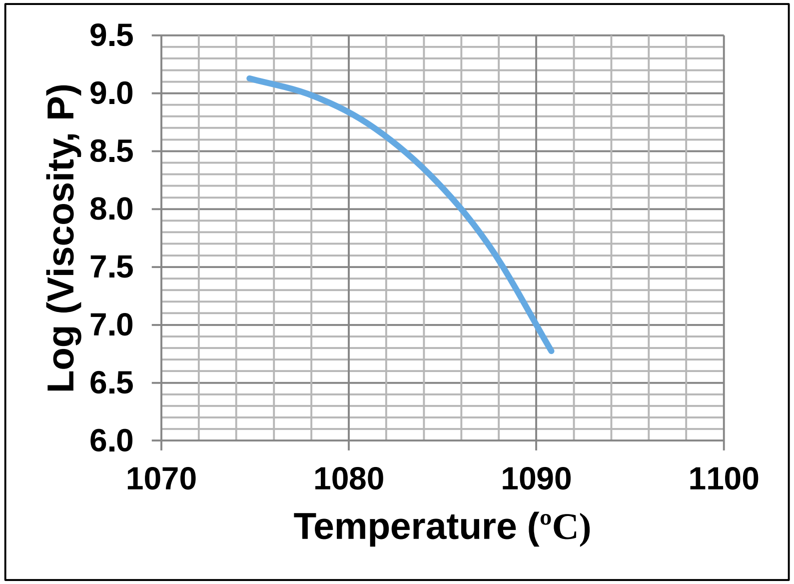


Flow evaluation

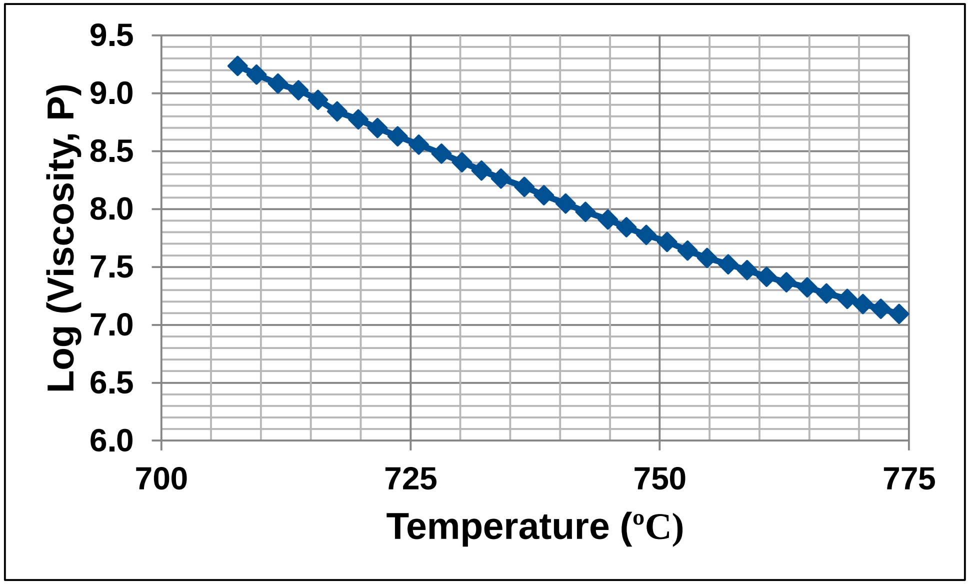
Frit A

Frit B

Viscosity curves in softening range

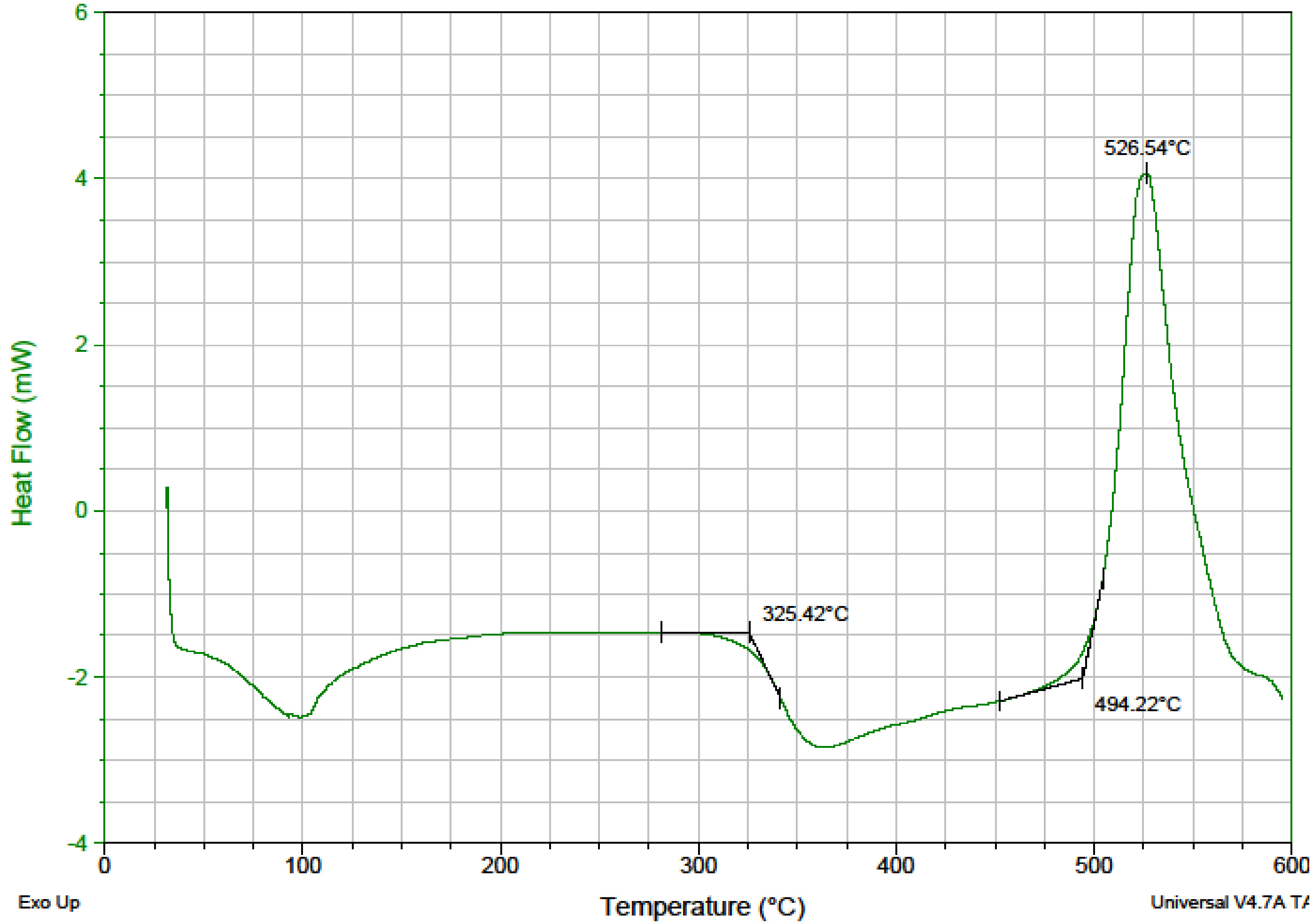


Frit A
after firing @ 900º-1hr

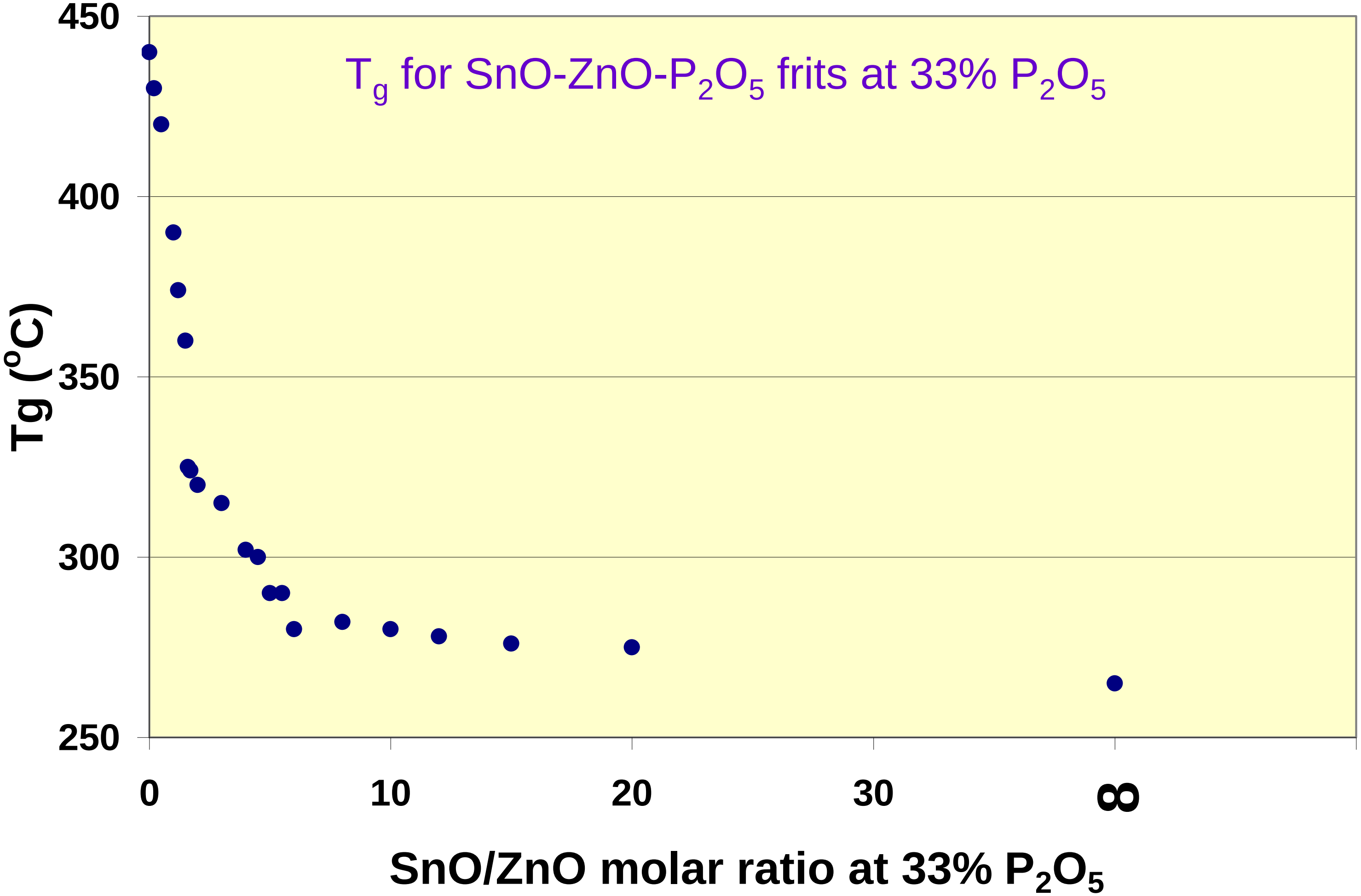


Frit B
after firing @ 800º-1hr

Temperature interval between T_g and T_x (onset) is best comparative predictor of flow



T_g is highly composition sensitive



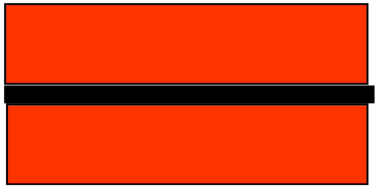
Expansion compatibility

Expansion compatibility

- Mismatch stresses from CTE differences can result in seal failure either during sealing, or in subsequent service.

- Measurement of mismatch

Butt seal

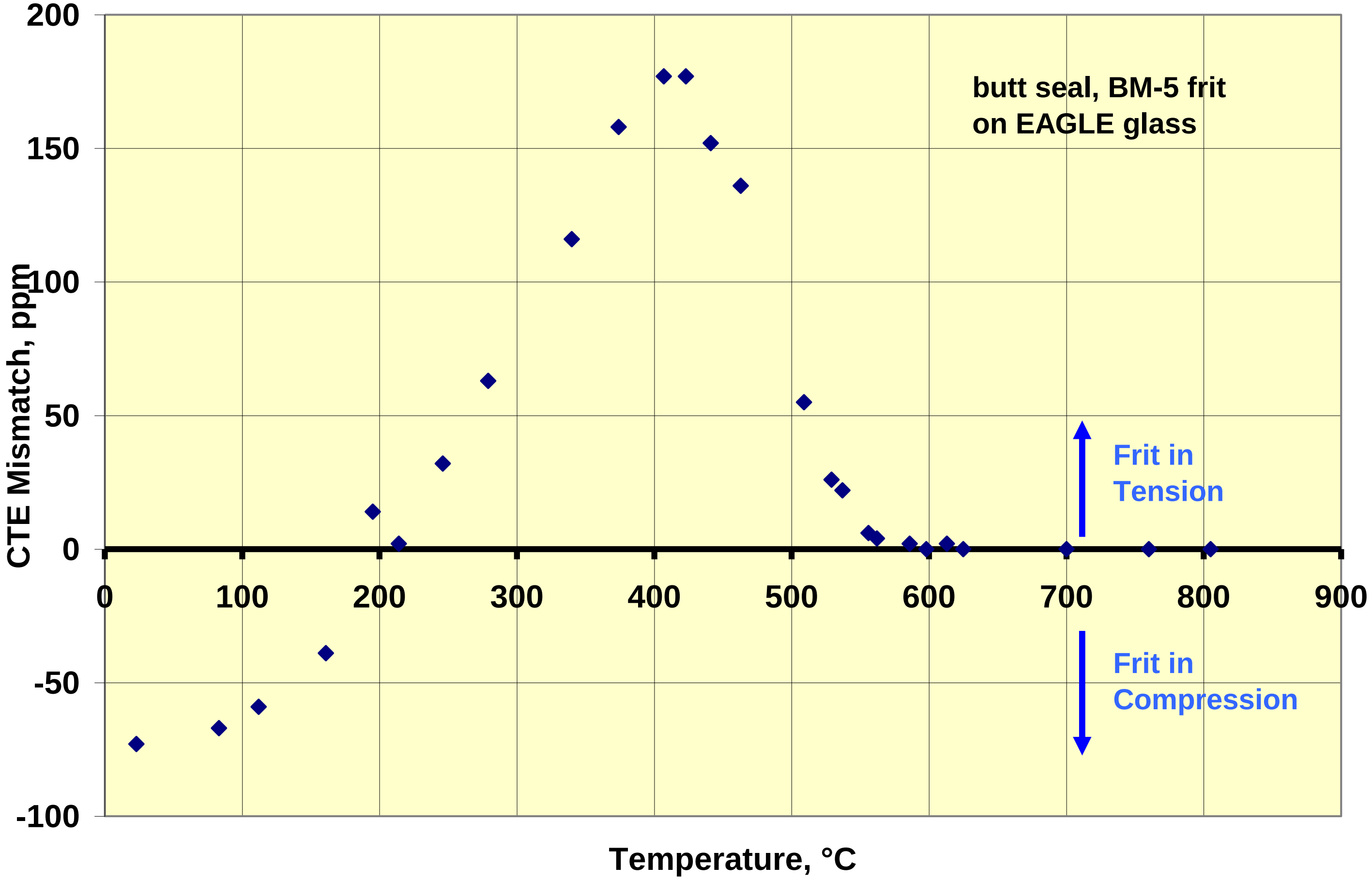


Inverse sandwich seal

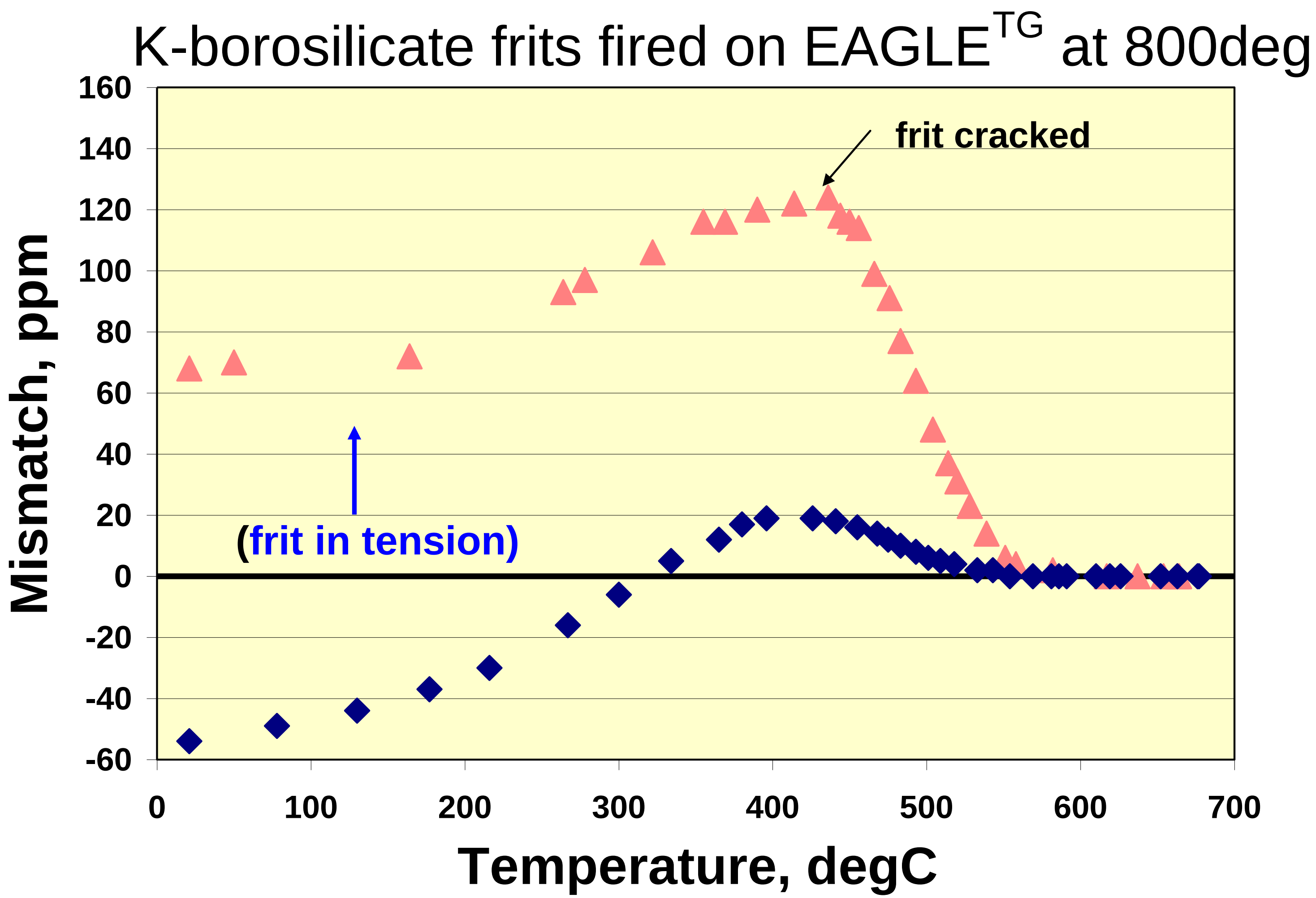
Expansion mismatch (δ) = $\Delta T\,(\alpha_f - \alpha_g)$ ⇒ residual stress, residual strain

Selection criterion:
Expansion compatibility: microreactor frit

- Perfect expansion match between a frit and a substrate is unlikely (different curvatures to expansion curve)



Expansion compatibility



CTE compatibility: use of fillers

- Fillers are added to adjust CTE of base fit

- Types of fillers
  - **Additive** – depend on Rule of Mixtures
  - **Inversion**
    - depend on volume change associated with phase transformation to adjust CTE
    - difficult to retain hermeticity because of localized microcracking
    - $PbTiO_3$, $[Co,Mg]_2 \cdot P_2O_7$

Effect of filler additions

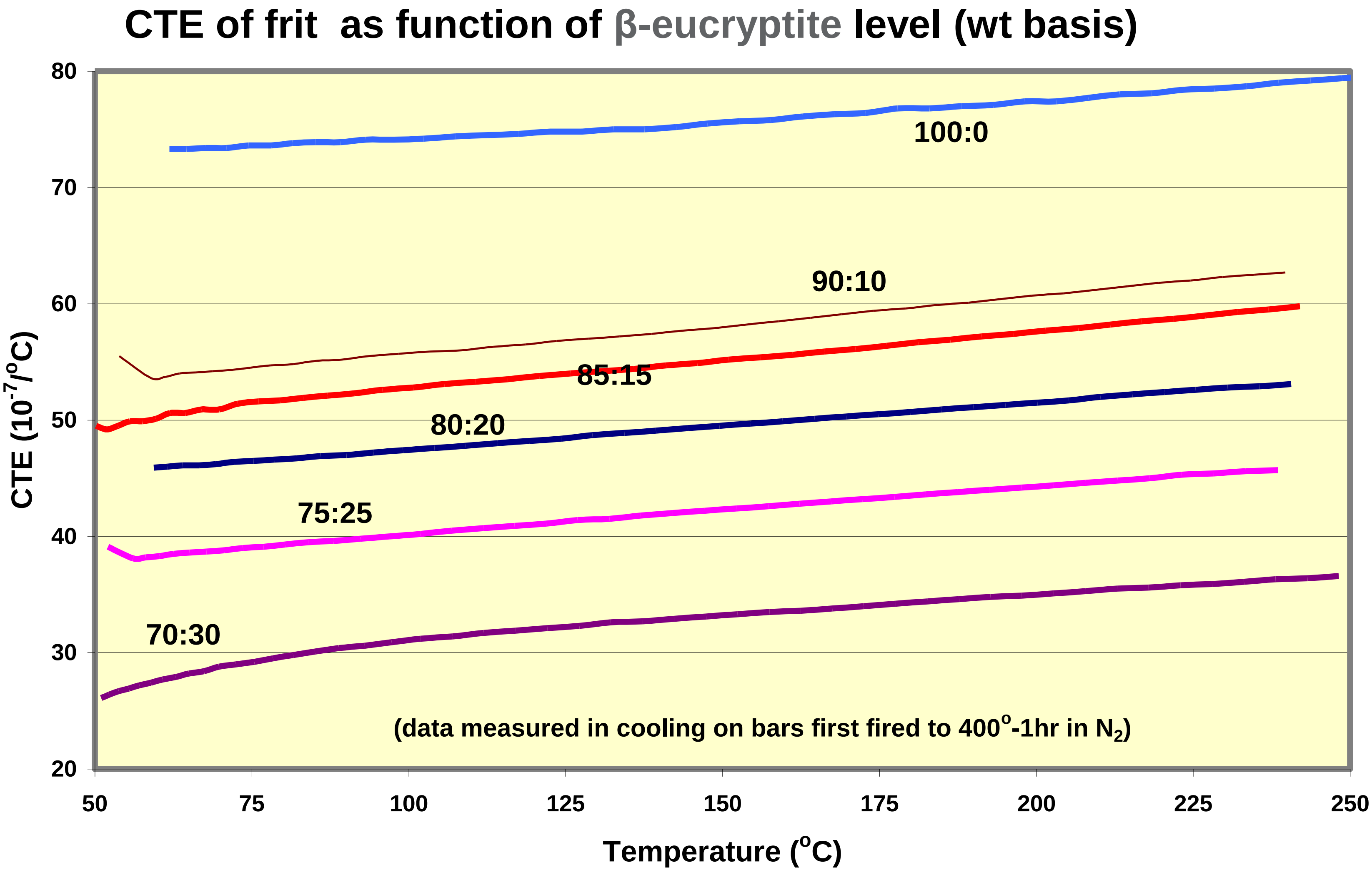
- Will adjust CTE, $\alpha = \dfrac{\alpha_1 K_1 V_1 + \alpha_2 K_2 V_2}{K_1 V_1 + K_2 V_2}$ (for additive fillers)
- Will affect flow, and raise viscosity (and most likely, sealing temperature)

V-phosphate frit with different filler loadings fired at 380°-1h

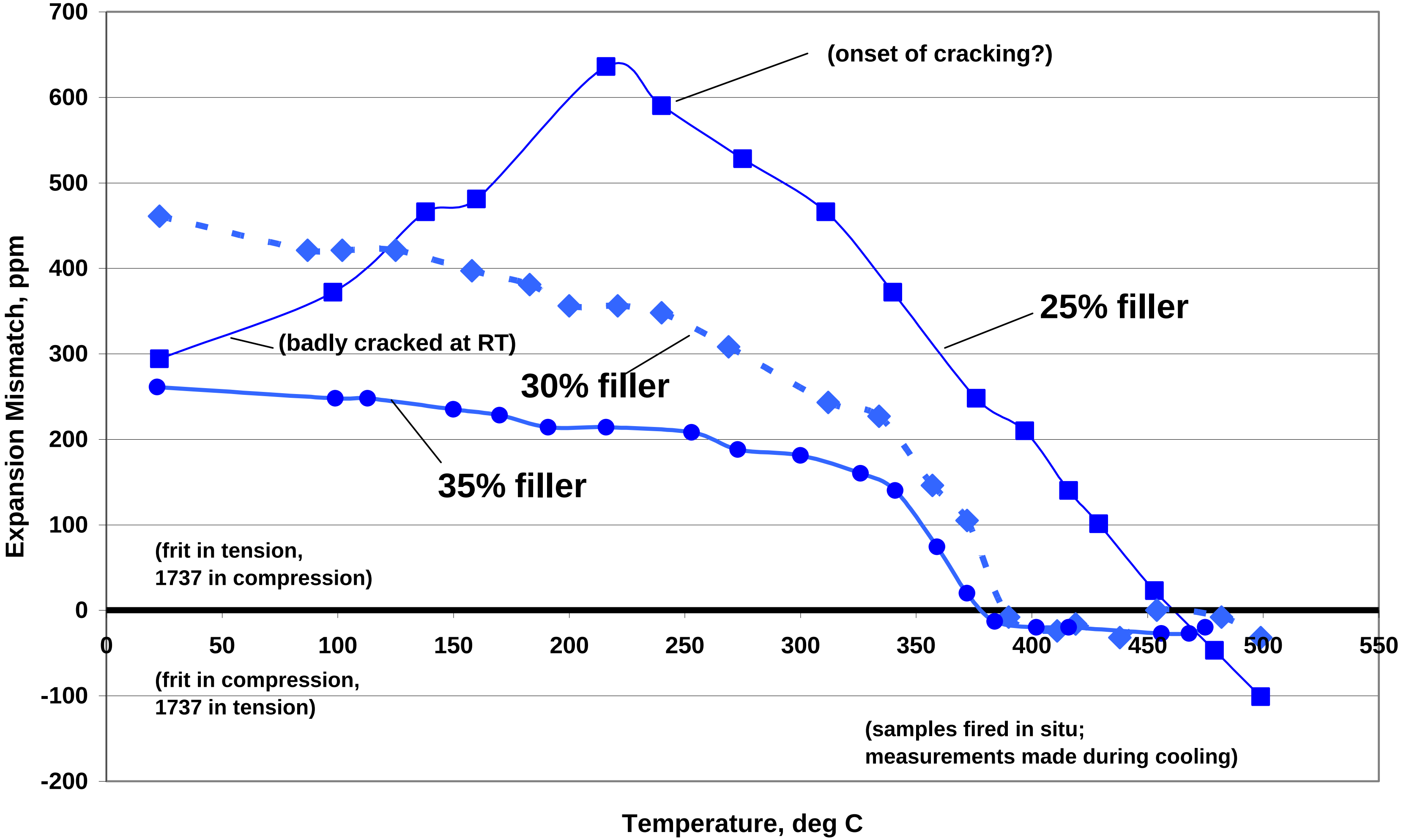
Possible additive-fillers

- β-eucryptite, LAS glass-ceramic, $Li_2O \cdot Al_2O_3 \cdot 2SiO_2$ (intrinsic) CTE = -10×10^{-7}/degC
- Stuffed β-quartz, ZnAS glass-ceramic, CTE = 0×10^{-7}/degC
- β-spodumene, LiZnMgAS, CTE = $+10 \times 10^{-7}$/degC
- ZWP, $Zr_2(WO_4)(PO_4)_2$, CTE = -30×10^{-7}/degC
- Leucite, $K_2O \cdot Al_2O_3 \cdot 2SiO_2$, CTE = 200×10^{-7}/degC
- (Stabilized) ZrO_2, CTE = 110×10^{-7}/degC

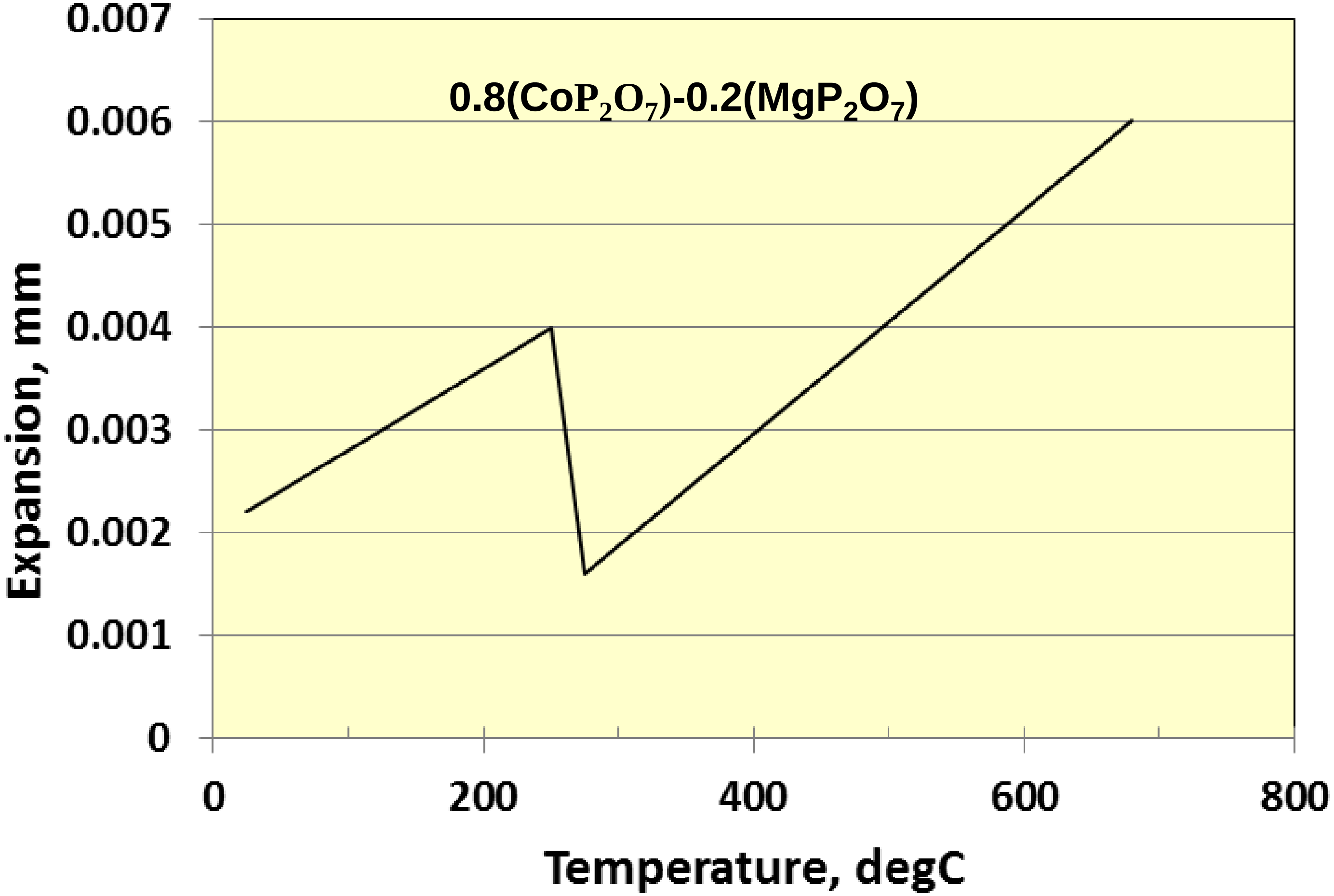
Additive filler – β-eucryptite



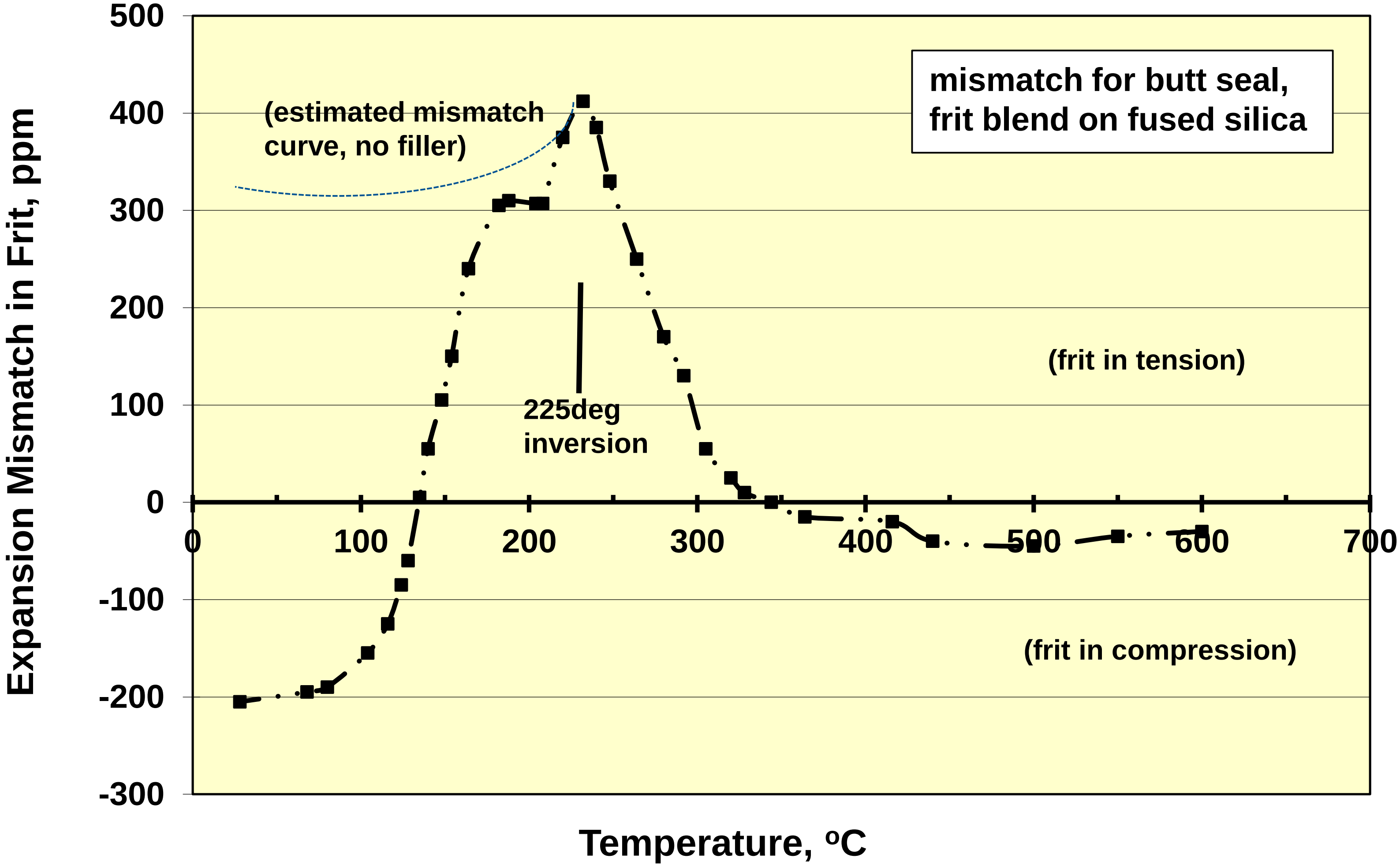
Expansion compatibility with display glass



Inversion filler - $(Co,Mg)_2 \cdot P_2O_7$



Inversion filler in frit



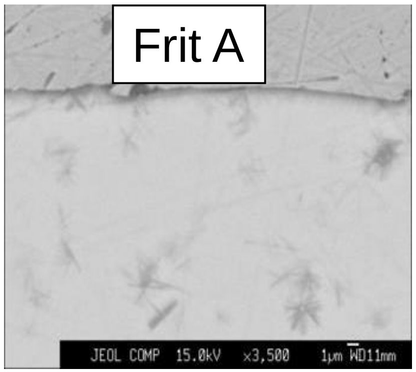
Service temperature

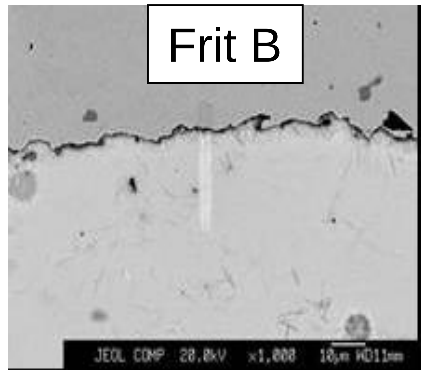
Service temperature

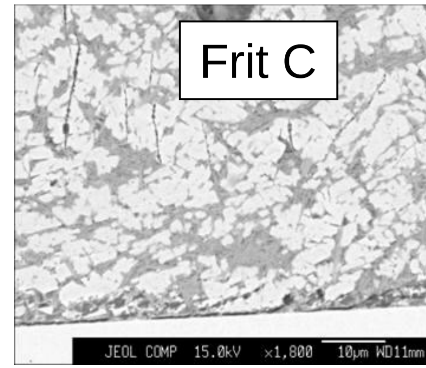
- Considerations
  - Frit viscosity (should be ≥10^{10} P for dimensional stability)
  - Stable chemistry and microstructure needed for long survival times
  - No reaction with substrate
  - Soft vs hard seal –stress relief during cooling vs. dimensional stability

Frit microstructure may change at high service temperatures

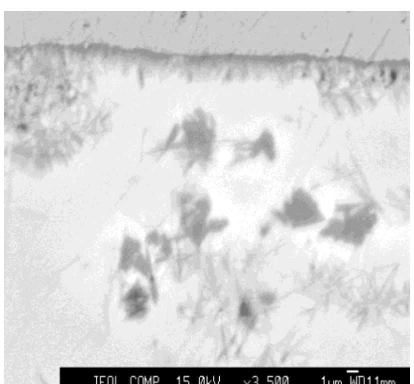
As-fired (850º-1hr)

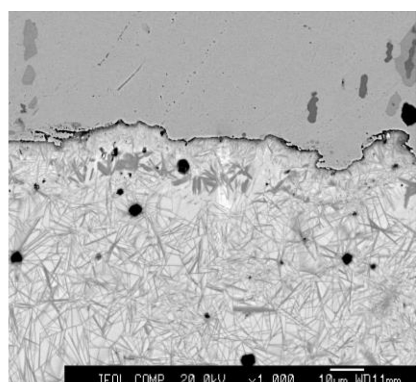


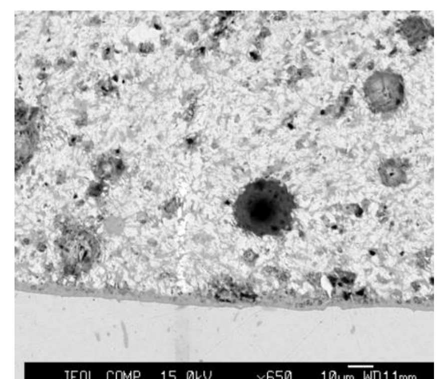




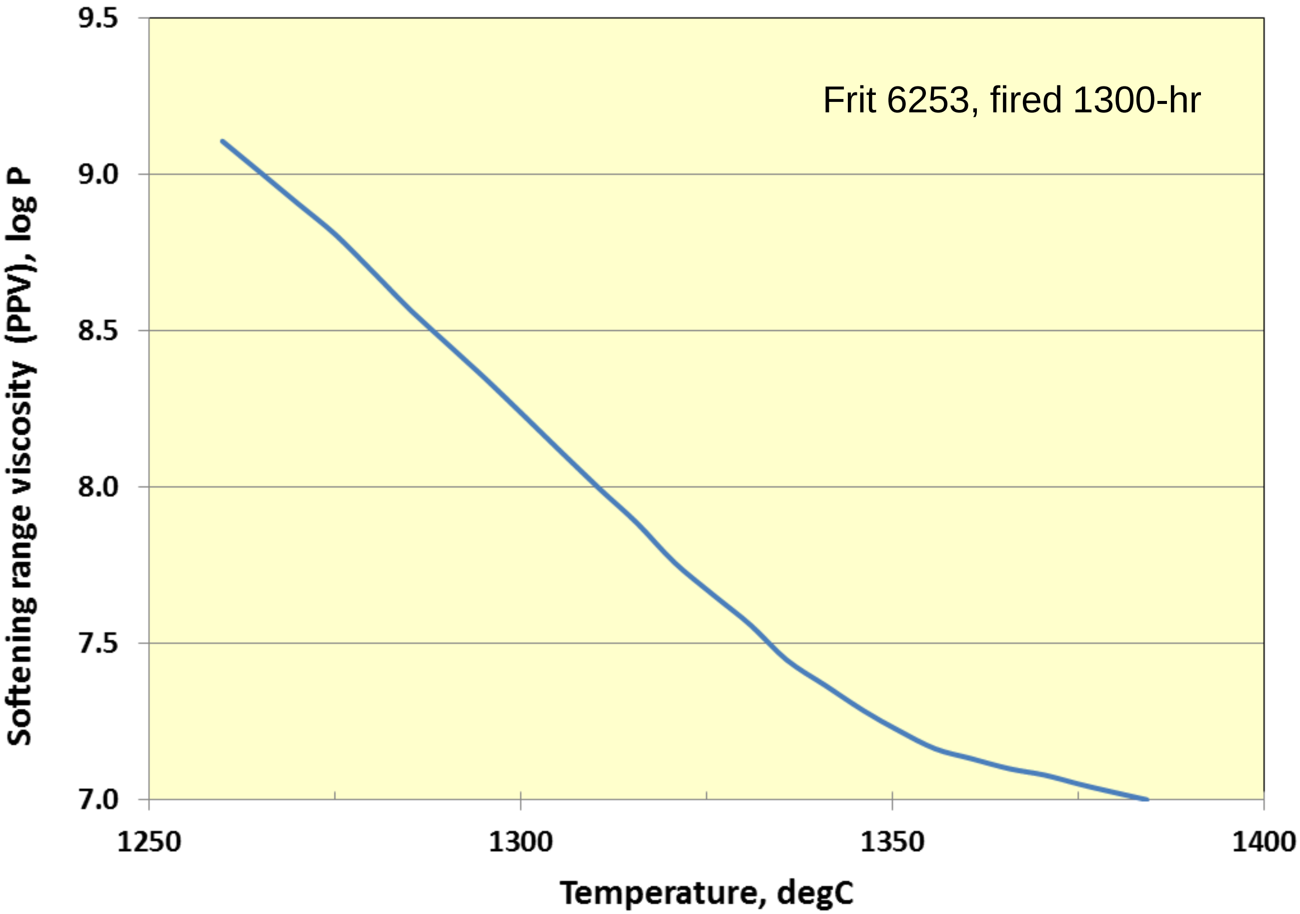
After aging (167hrs at 725º)

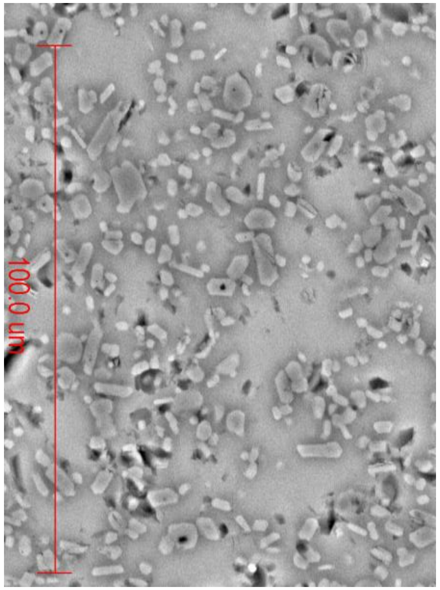




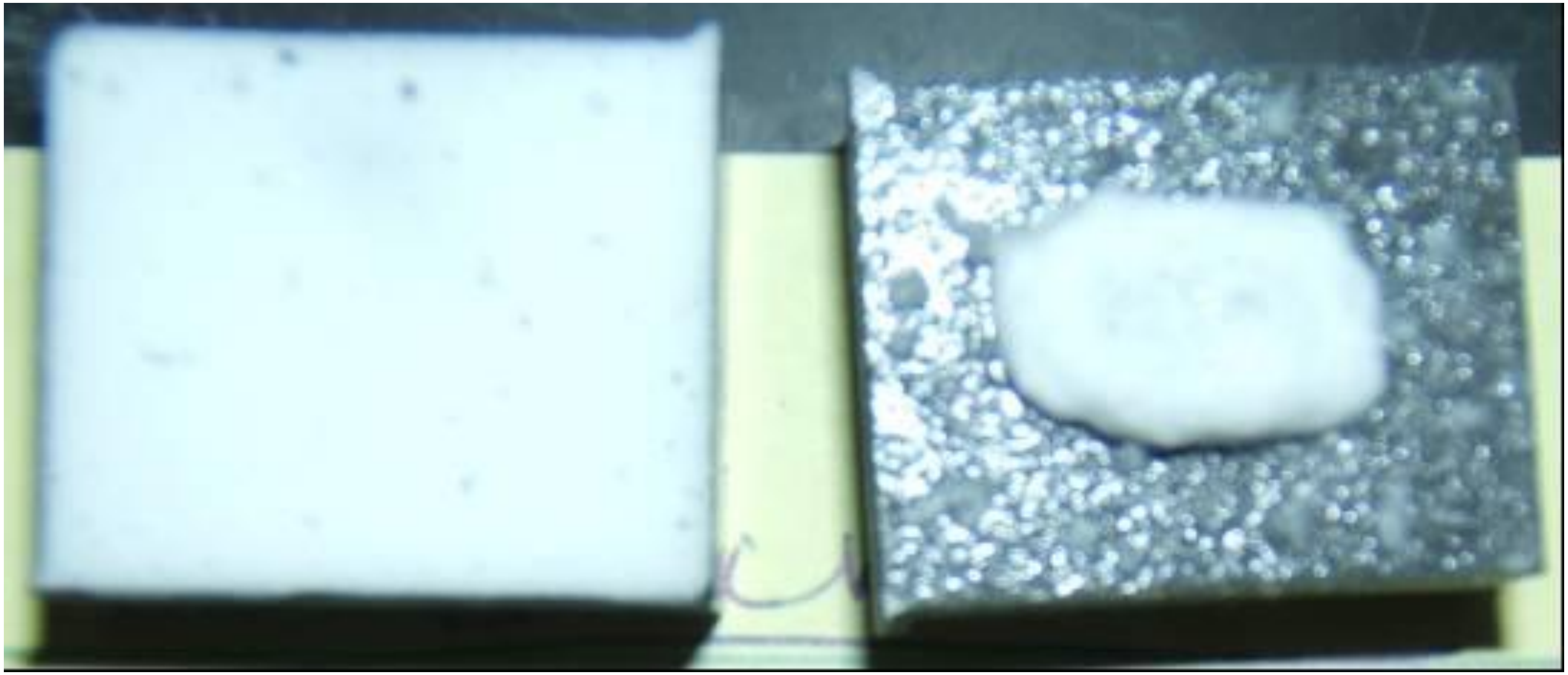


High temp frit coating for Pt
(must withstand exposure at 1200deg)





Coating for SiC furnace tubes



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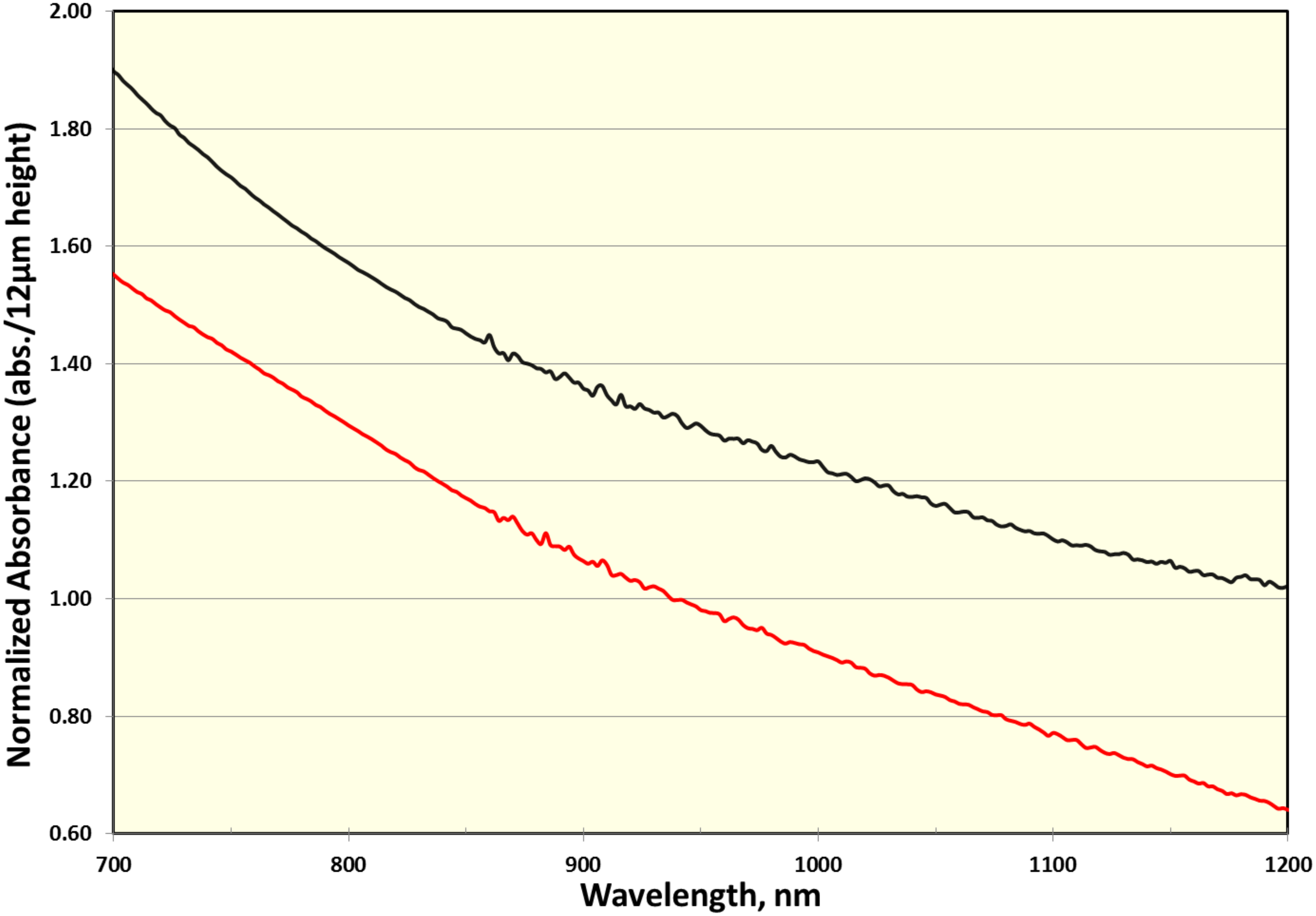
Thermal aging samples (120hrs @1500°)

Other criteria

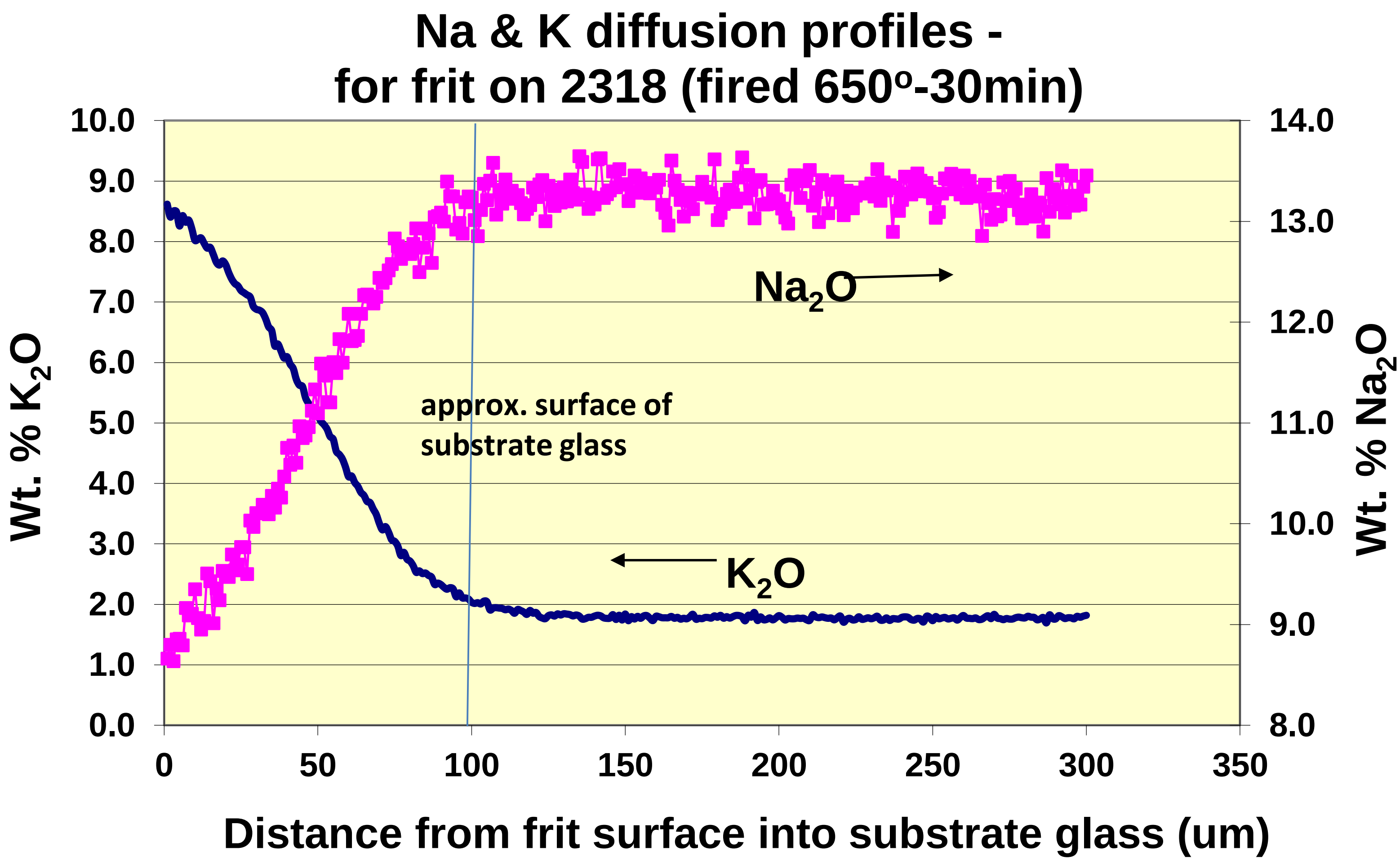
Selection criterion: aqueous durability (frits for insulating windows)

Aqueous durability
48hr, 90deg DI H2O
(380-1h air)

Near-IR Absorbance



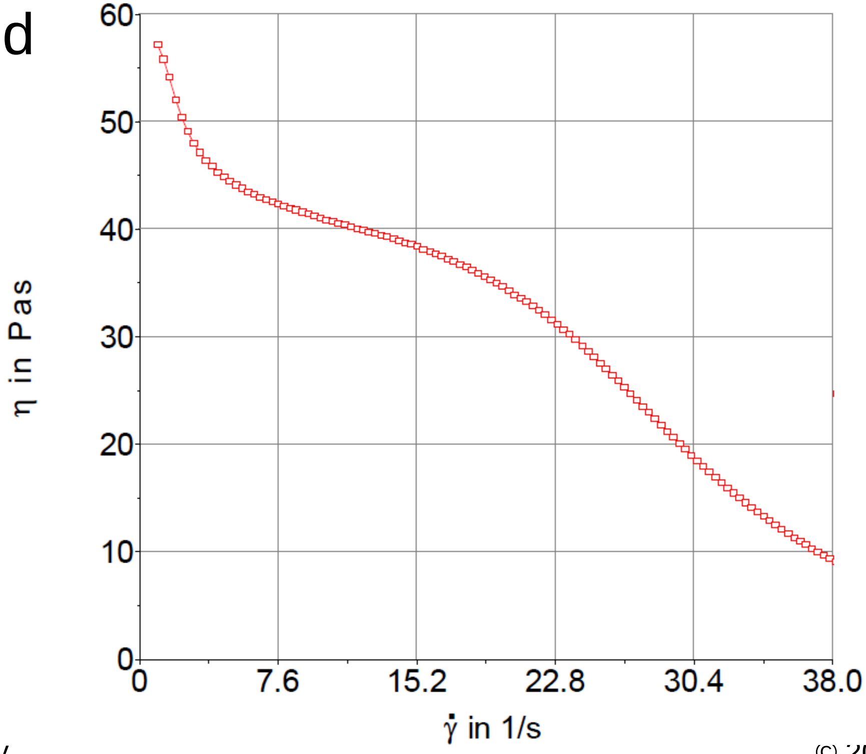
Selection criterion: compressive surface layer for strength



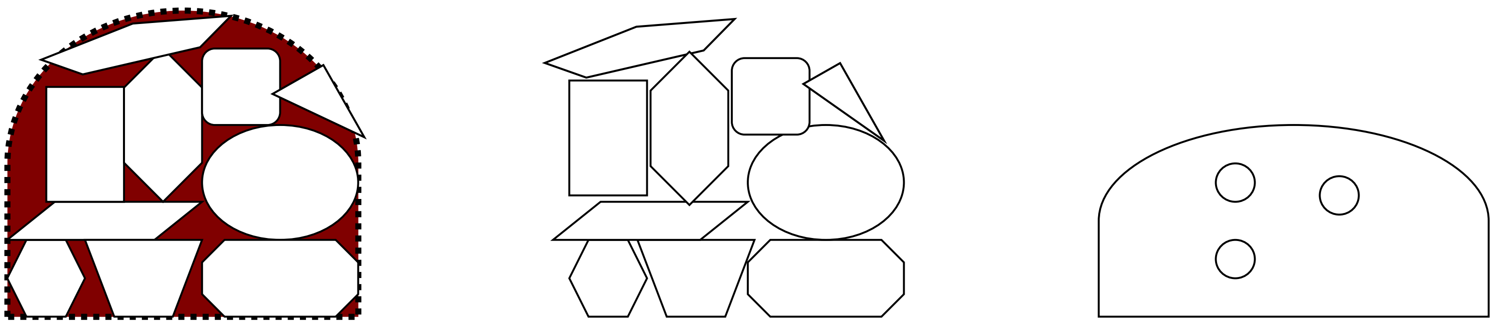
Processing of frits

Frit pastes

- Although frits may be applied by a variety of techniques (screen-printing, doctor-blading, nozzle dispensing, etc), they are always applied as a paste or ink rather than as a powder.
- Paste = frit powder + solvent + binders + dispersants + surfactants
- The paste is designed to exhibit a specific rheology needed for the dispensing method



Changes in frit paste with temperature

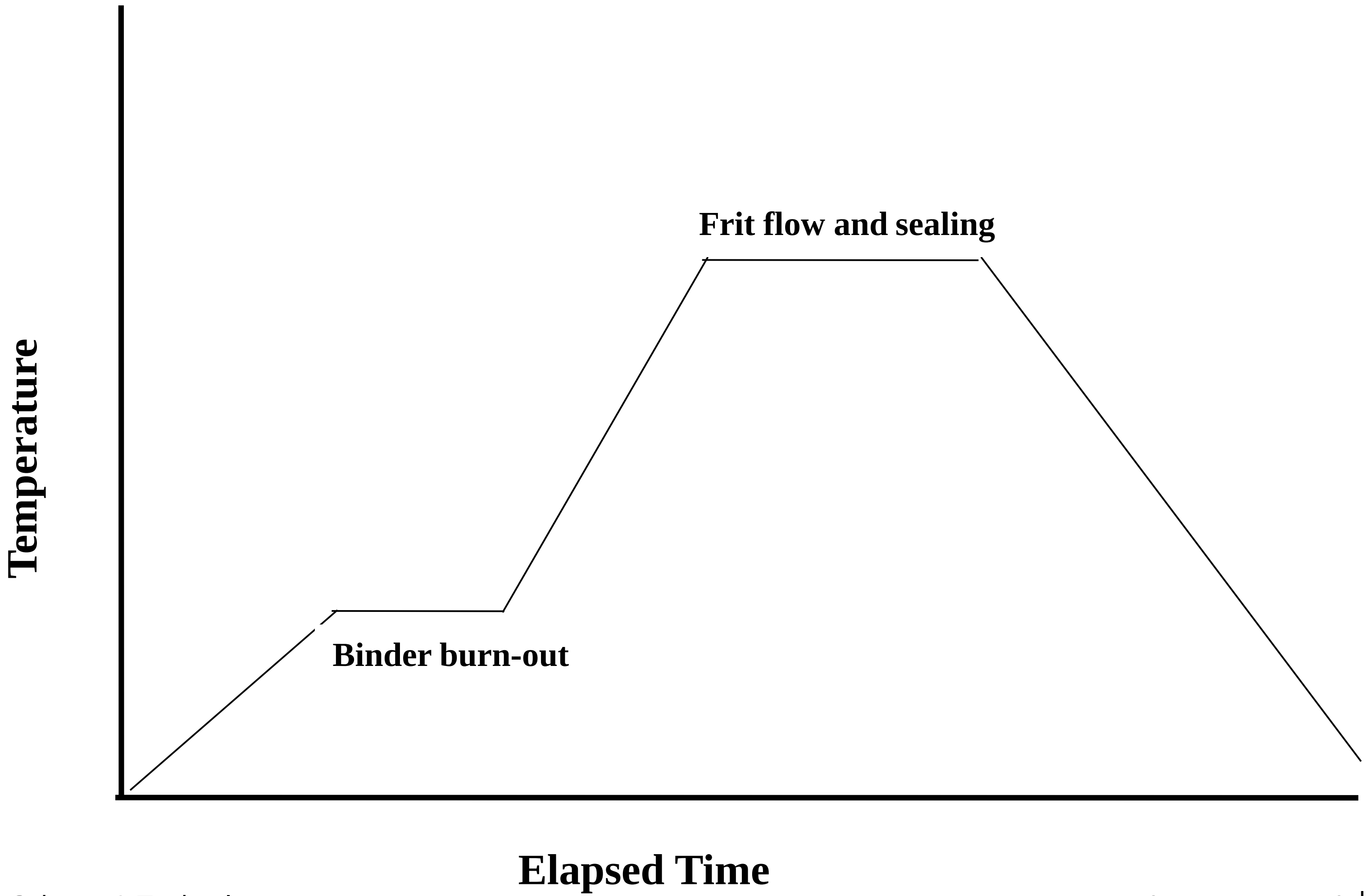


Dispensed paste

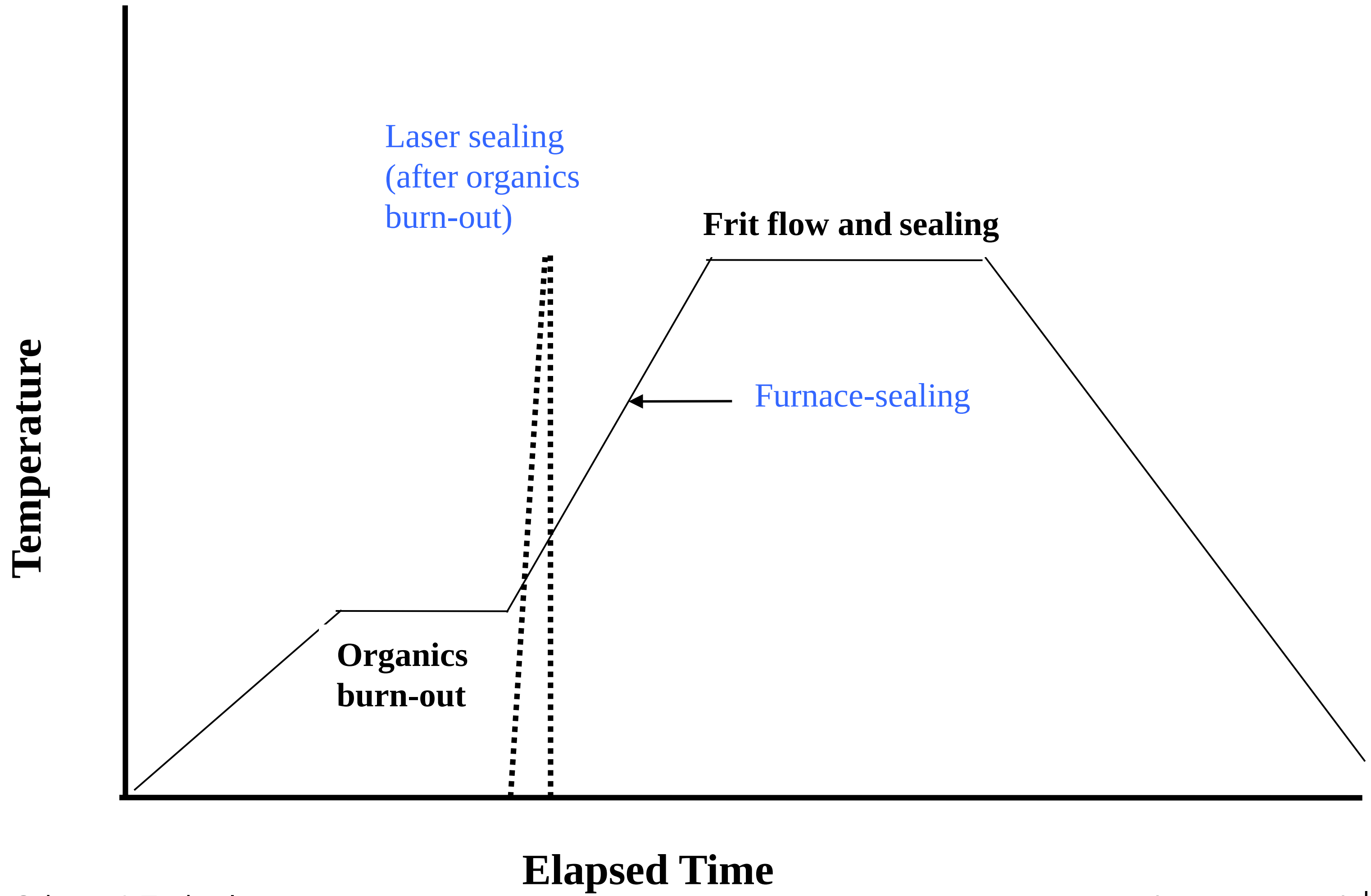
After organic burn-out (300-325º)

After frit softening and flow (500-600º)

Furnace sealing

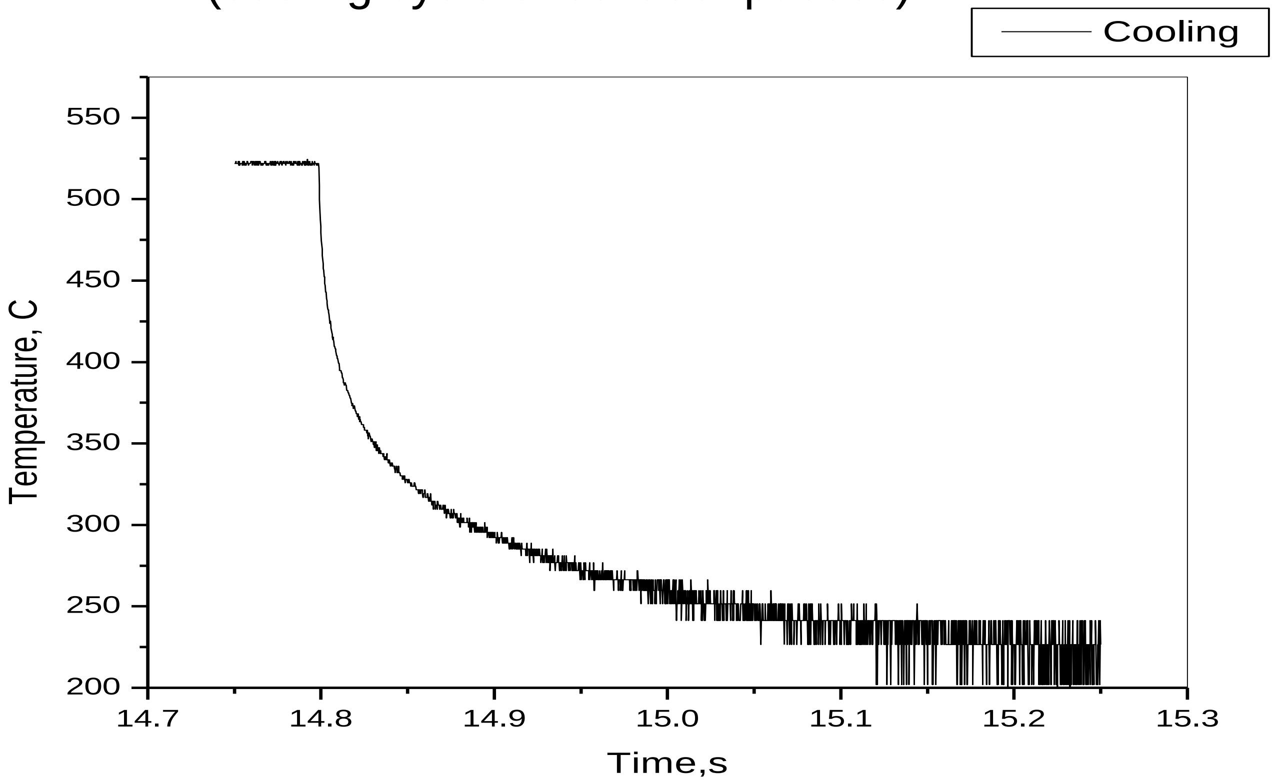


Processing comparison

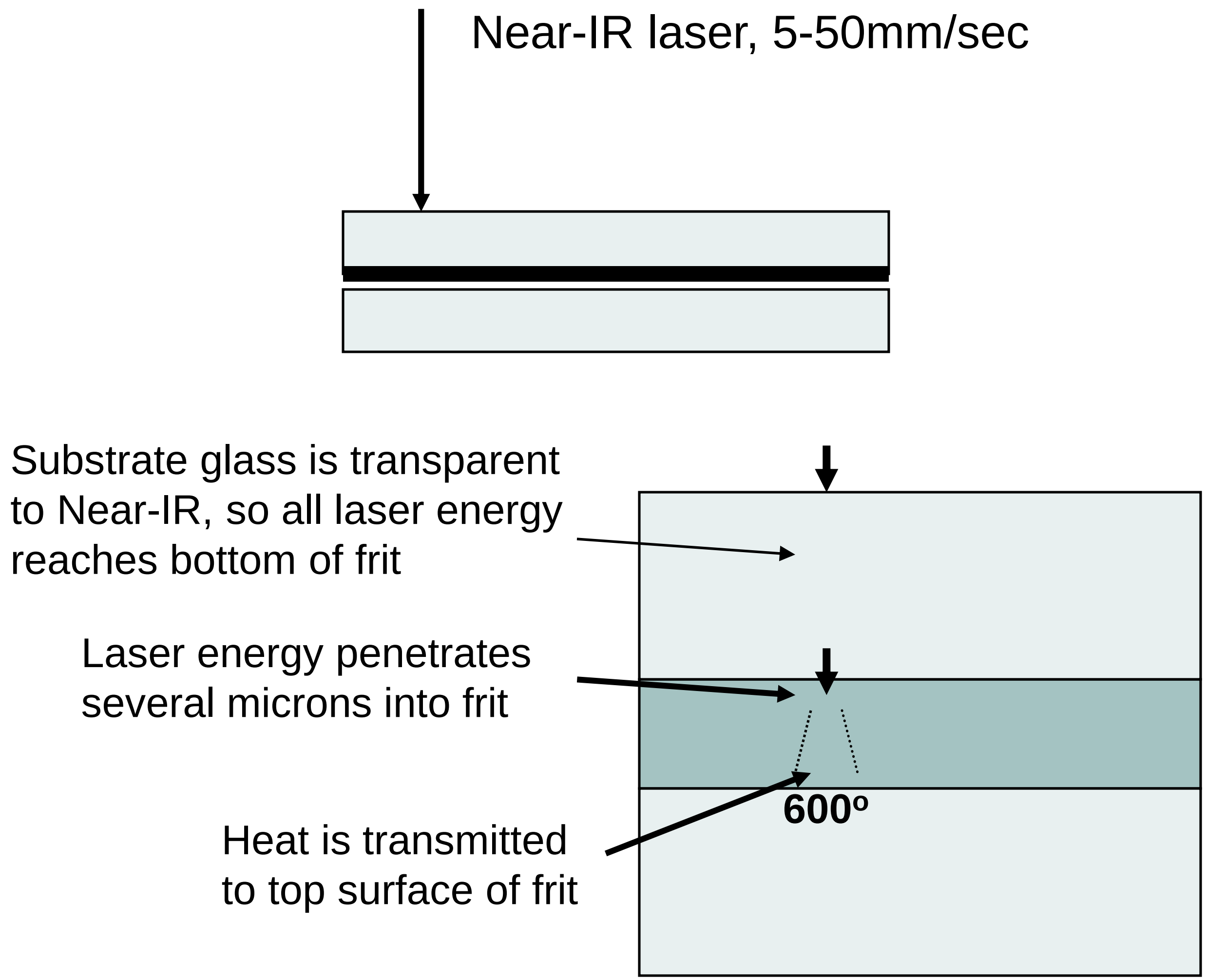


Laser-sealing process is very fast

(cooling cycle once laser passes)



Close-up look at laser-sealing



Acknowledgements

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