Web Course
Physical Properties of Glass

1. Properties of Glass Melts
2. Thermal Properties of Glasses

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Melt and Glass Properties

- Viscosity
- Surface Tension
- Thermal Expansion
- Heat Capacity
- Thermal Conductivity

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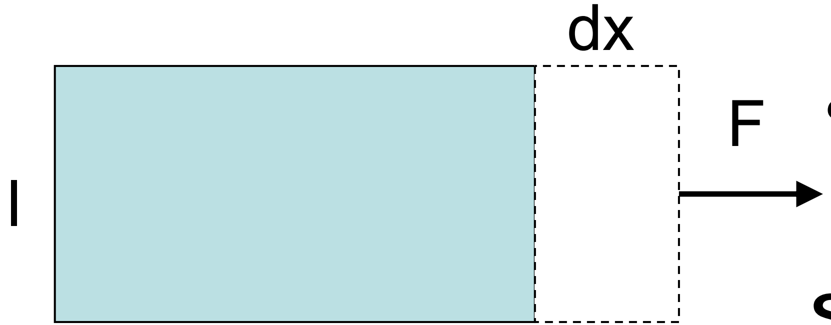
Surface Tension

Thermodynamic definitions

- To create a stable interface between two phases, the free energy of formation of the interface must be positive (to avoid miscibility.)



Work (W) done to create new area (dA=l·dx):

$$W = F \cdot dx$$

***Surface tension (γ)** resists the creation of new area:*

$$\gamma = F/l \text{ , and so } W = \gamma \cdot dA$$

Units for γ: ergs/cm^2 (or dyn/cm), J/m^2 (or N/m)

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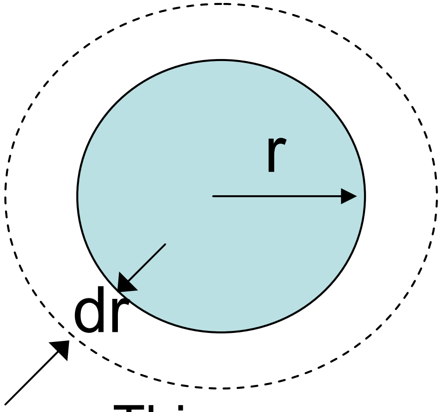
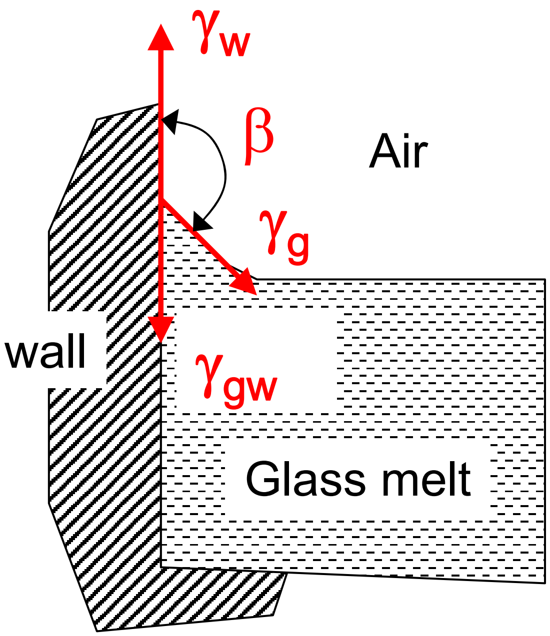
Young-LaPlace Equation

- Surface tension resists bubble expansion, so work is required to expand bubble radius



$$\Delta P \cdot \Delta V = \gamma \cdot dA$$
$$\Delta P \cdot (4\pi r^2 \cdot dr) = \gamma \cdot (8\pi r \cdot dr)$$
$$\Delta P = 2\gamma / r$$

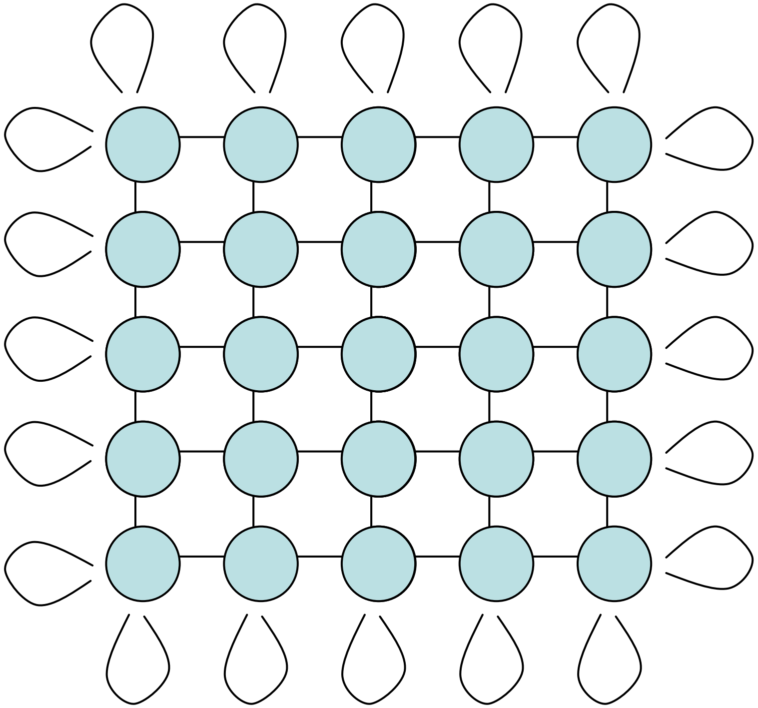
- This pressure differential explains:
  - Capillary rise
  - Increased vapor pressure/solubility of curved surfaces
  - Wetting behavior (Young-Dupree equation)



$$\gamma_w = \gamma_{gw} + \gamma_g \cdot \cos(\pi - \beta)$$

What is the source for ‘surface energy’?

- Consider a hypothetical lattice



‘Surface atoms’ have lower average coordination numbers (CN) than ‘bulk atoms’; this affects lattice energy (V) which depends on bond energy (ε) and number of bonds (CN).

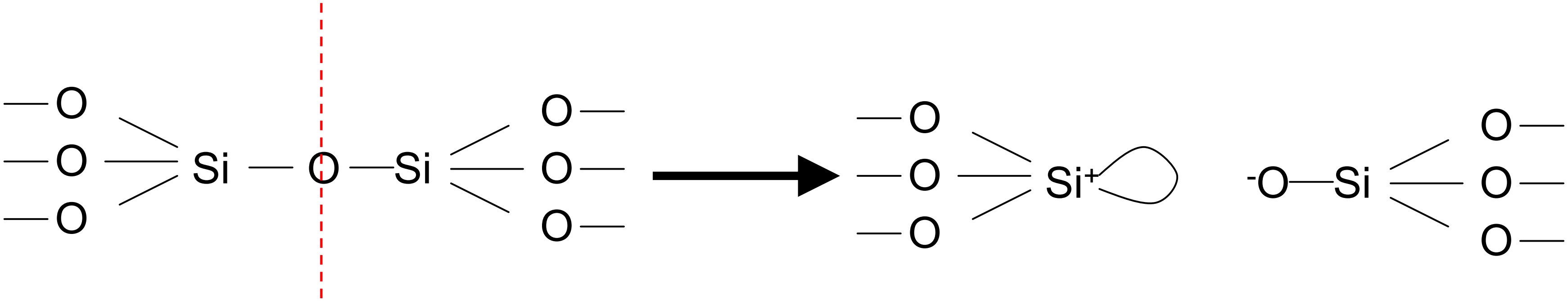
$$V_{\min}^{bulk} = \left(\frac{CN_{bulk}}{2}\right)\varepsilon, V_{\min}^{surface} = \left(\frac{CN_{surf}}{2}\right)\varepsilon$$

$$Surface\ Energy \equiv V^{surface} - V^{bulk} > 0.$$

$$Note: \quad \frac{CN_{surface}}{CN_{bulk}} \approx 0.6 - 0.8$$

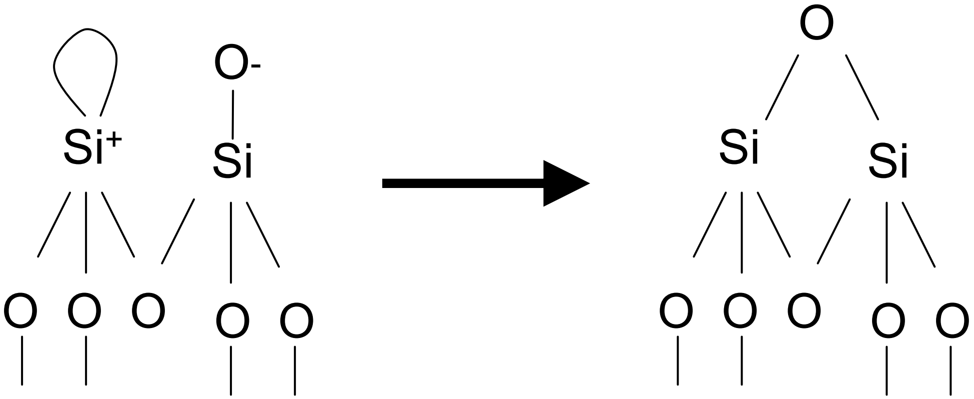
Surface energy arises from the incomplete coordination (or charge compensation) of surface atoms compared to bulk atoms.

Does fracture create dangling bonds?



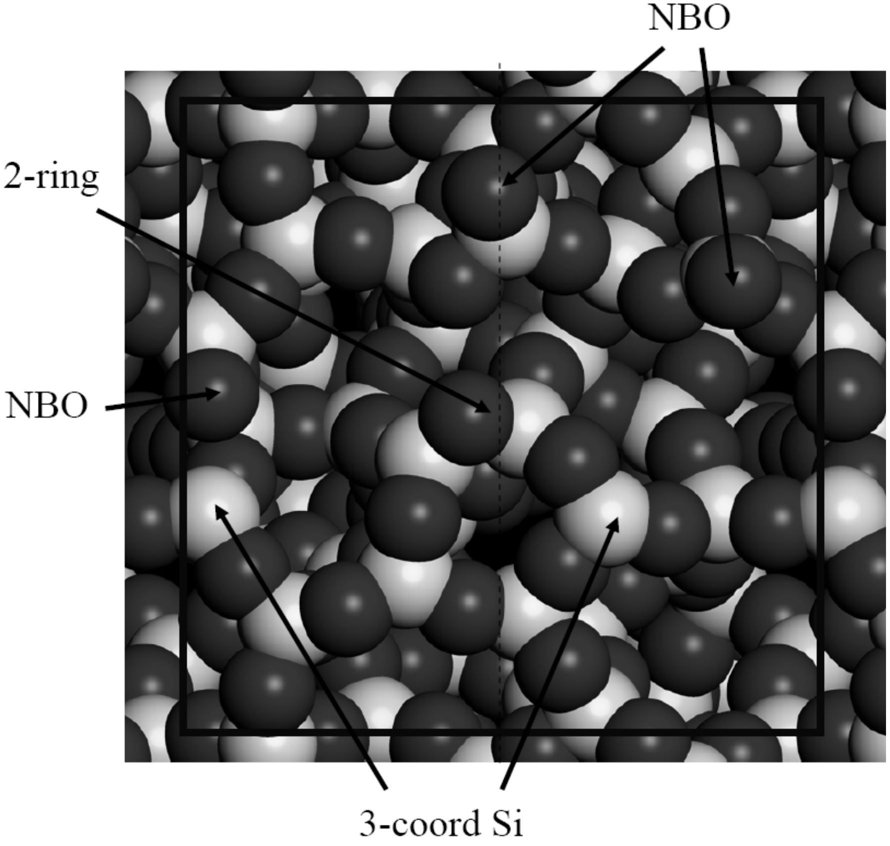
Reconstruction is more likely:

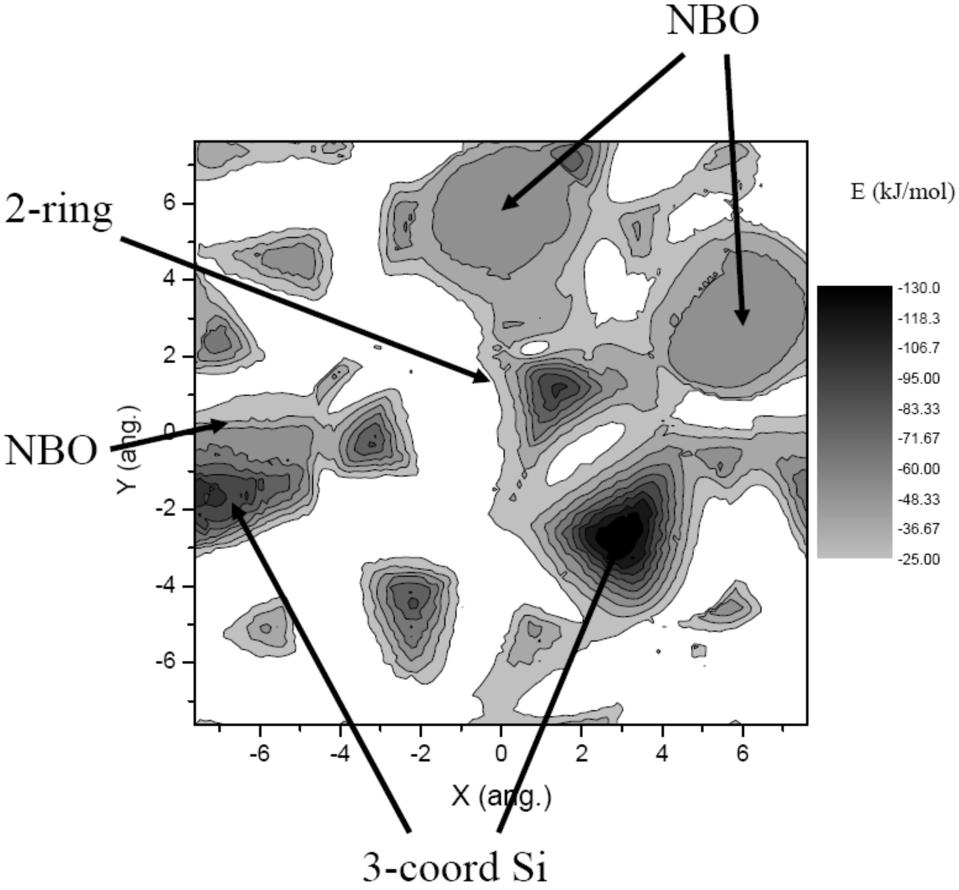
No ESR evidence: Hochstrasser and Antonini (1972)



Edge-shared tetrahedra are commonly sound on silica surfaces

MD Simulation of silica glass fracture surface



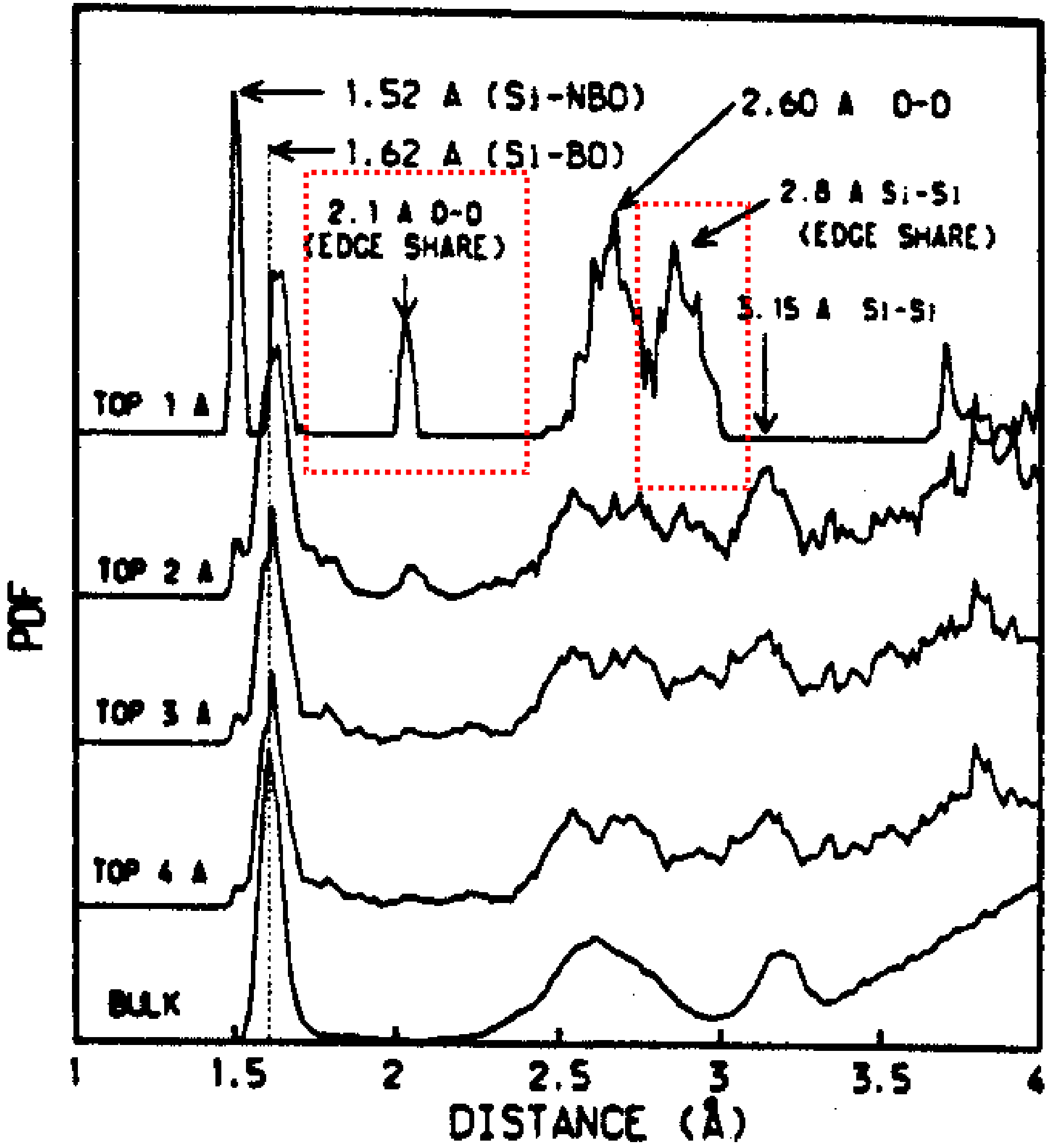


EA Leed et al., Phys Rev B 72[15] 155427 (2005)

‘Modified’ surfaces extend several monolayers

Pair-distribution functions from a silica fracture surface from a molecular dynamics simulation- compared to the ‘bulk’ PDF (bottom)

Levine et al., *J. Chem. Phys*. **86** 2997 (1987).

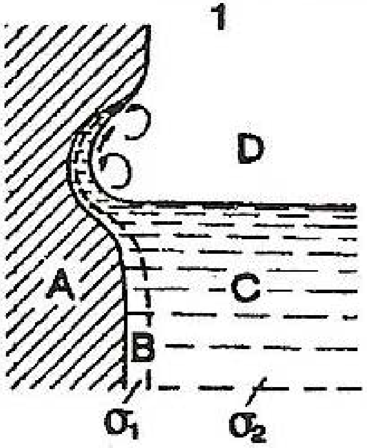


Surface Tension- melts

- Smoothing sharp corners (fire polishing)
- Contraction of fibers during fiber-drawing
- Equilibrium thickness of ‘float glass’ melts
- Adhesion and wetting (contact angles) with forming materials
- Penetration of glass melts into refractory pores
- Nucleation and growth of gas bubbles in the melt
- Eddy currents at melt surfaces due to local differences in γ
  - Compositional gradients near refractory walls create γ-gradients which drive melt currents- undercutting refractories at ‘melt line’

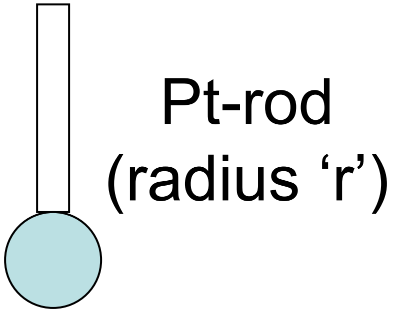
Eddy currents at melt surfaces due to local differences in γ

- Compositional gradients near refractory walls create γ-gradients which drive melt currents- undercutting refractories at ‘melt line’



Metal line corrosion: 1) often: $\sigma_1 > \sigma_2$ and the bulk glass melt (low surface tension σ_2) flows from the surface of the melt to the wall and will submerge the melt enriched by dissolved refractory components (surface tension σ1). This surface tension gradient driven convection enhances the dissolution process.

Measuring Surface Tension



Droplet method:

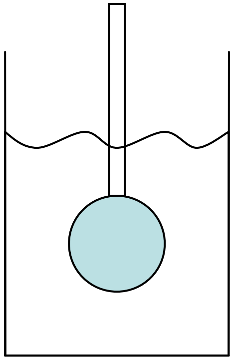
Measure weight (m·g) of melt drop that detaches from end of Pt-rod or tube:

$$\gamma = m \cdot g/(2\pi \cdot r)$$

Bubble-pressure method:

Measure pressure (Δp) required to blow a bubble from a melt (density ρ) with a Pt-capillary (radius r) inserted to a depth (l):

$$\gamma = r \cdot (\Delta p - g \cdot l \cdot \rho)/2$$



Ring method

Pt-wire ring (radius ‘R’) immersed in a melt, then pulled out with application of constant force (W); ‘a’ is correction factor..

$$\gamma = aW/4\pi \cdot R$$

Elongation of glass fiber

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From Beerkens, 1997

Surface Tension

Glass type	γ (mN/m)
S-L-S (flint/float)	310
Brown bottle	296
E-glass	315
TV-glass	248
water	72
mercury	550

Slight temperature dependence:
γ decreases 4-10 mN/m per 100°C increase for most common glasses

SO_3, Cr_2O_3, V_2O_5 all significantly decrease γ, as does water

MgO, Al_2O_3 increase γ

- Low surface tension melts may foam

Na_2SO_4 (liq) has lower surface tension (266 mN/m) than an SLS melt- Na_2SO_4 (liq) spreads on top of melt (continuous glassmelting tank operation) where it wets and dissolves unmelted sand….

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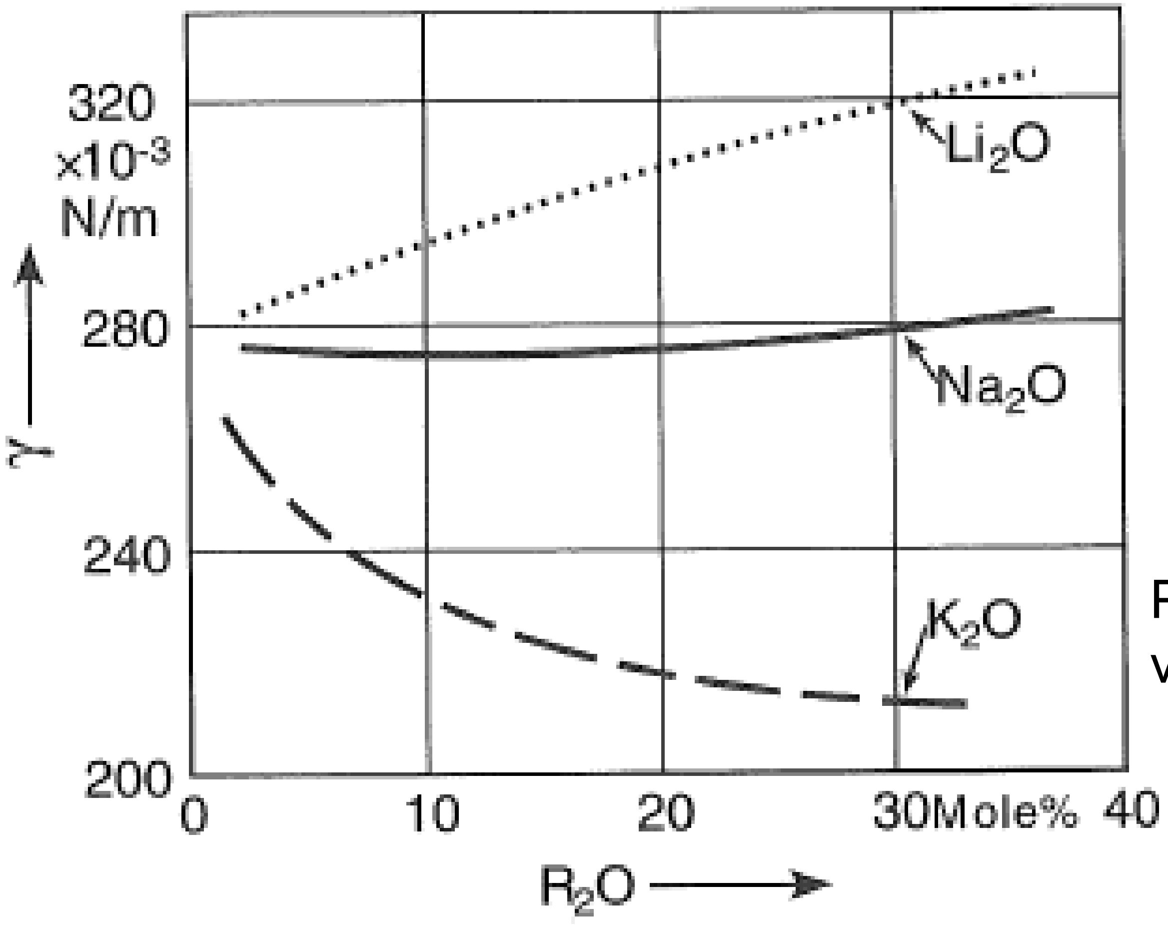
Compositional Effects on Surface Tension



Polarizable ions (K^+ vs. Na^+) reduce γ

Figure 9-19. Surface tension of alkali silicate melts at 1300°C. (After Shartsis and Spinner(34).)

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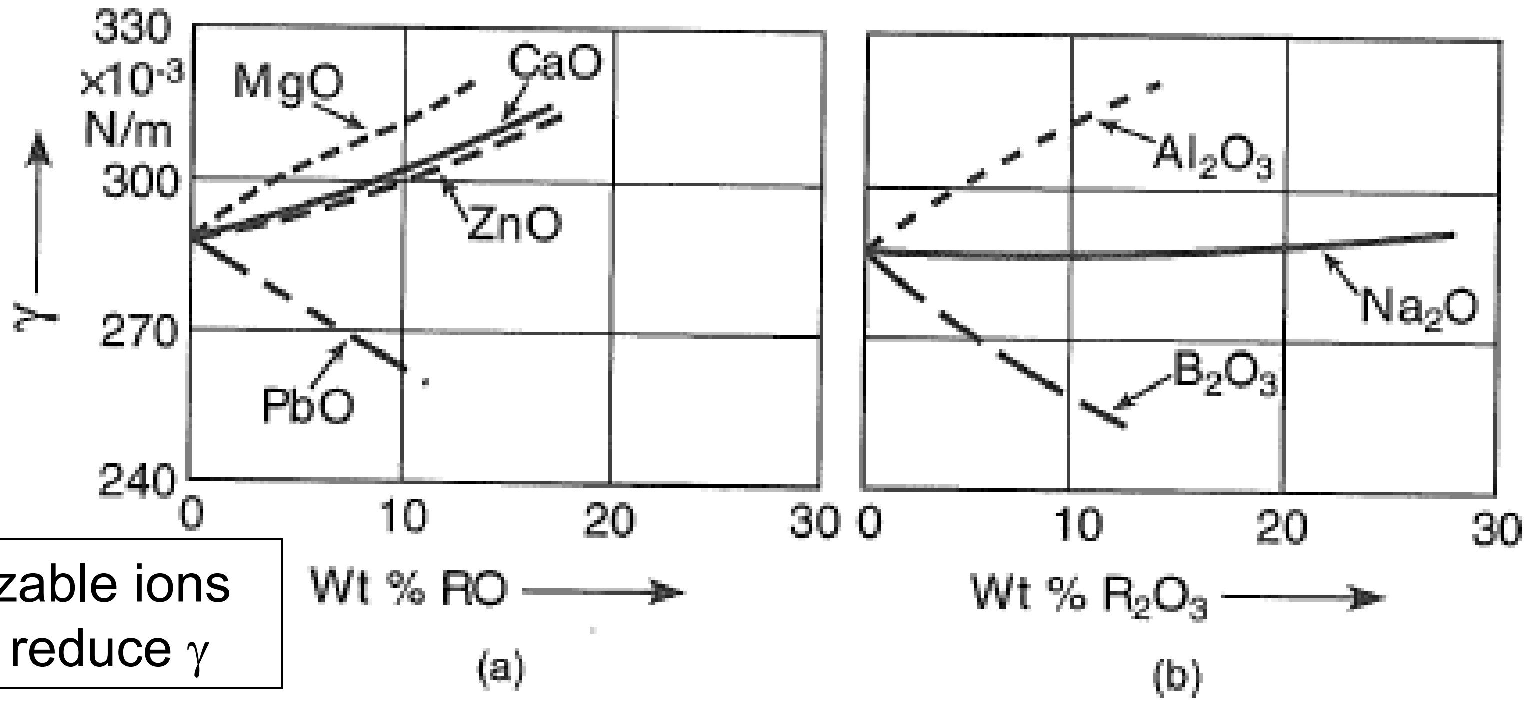
Compositional Effects on Surface Tension



Polarizable ions (Pb^{2+}) reduce γ

Figure 9-20. Surface tension of $(20-x)Na_2O \cdot xR_mO_n \cdot 80SiO_2$ (wt%) glasses at 1400°C. (After Shartsis and Spinner[34].)

Note: γ for B_2O_3 liquids is 80 mN/m at ~900°C (Varshneya, p. 243)

Compositional Effects on Surface Tension

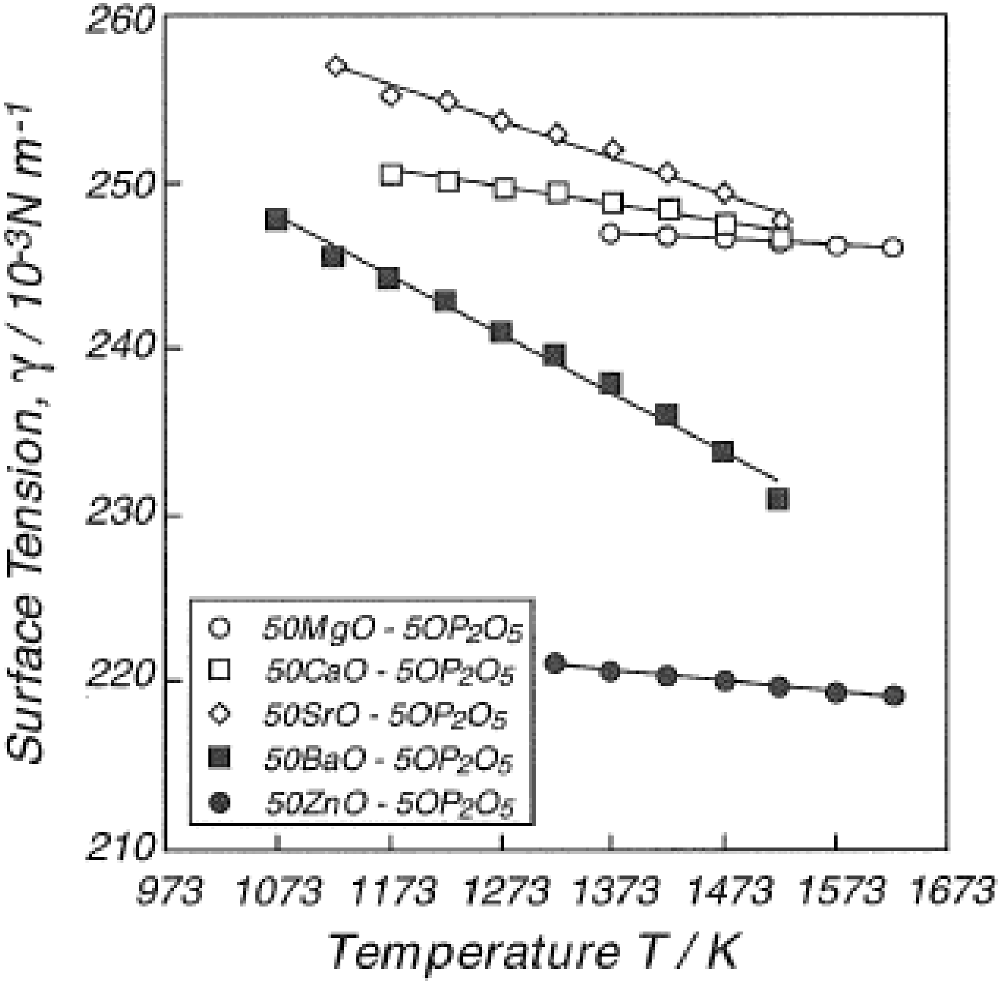


Figure 9-21. Temperature dependence of the surface tension of $50RO{\cdot}50P_2O_5$ glasses. (After Toyoda *et al*[35].)

Polarizable ions reduce γ and γ decreases with temperature

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Thermal Expansion

Definitions

Average volume expansion coefficient when temperature increases from T_1 to T_2

$$\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$$

The **instantaneous volume expansion coefficient** is given by

$$\beta_m = \frac{V_2 - V_1}{V_1\left(T_2 - T_1\right)}$$

The corresponding **linear expansion coefficients** (α) are obtained by replacing volume with length, e.g.

$$\alpha = \frac{\Delta l}{l_0 \Delta T}$$

Units: 10^{-7}/ºC, reported over designated temperature range

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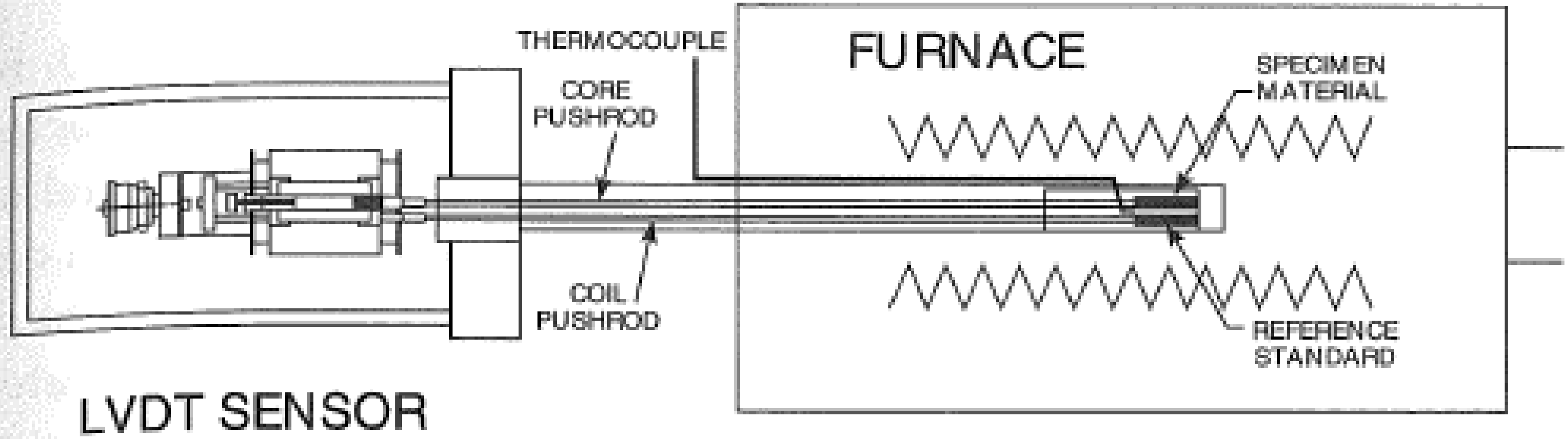

Figure 10-1. Schematics of a double pushrod differential dilatometer. (Courtesy: Theta Industries, Inc., Port Washington, NY.)

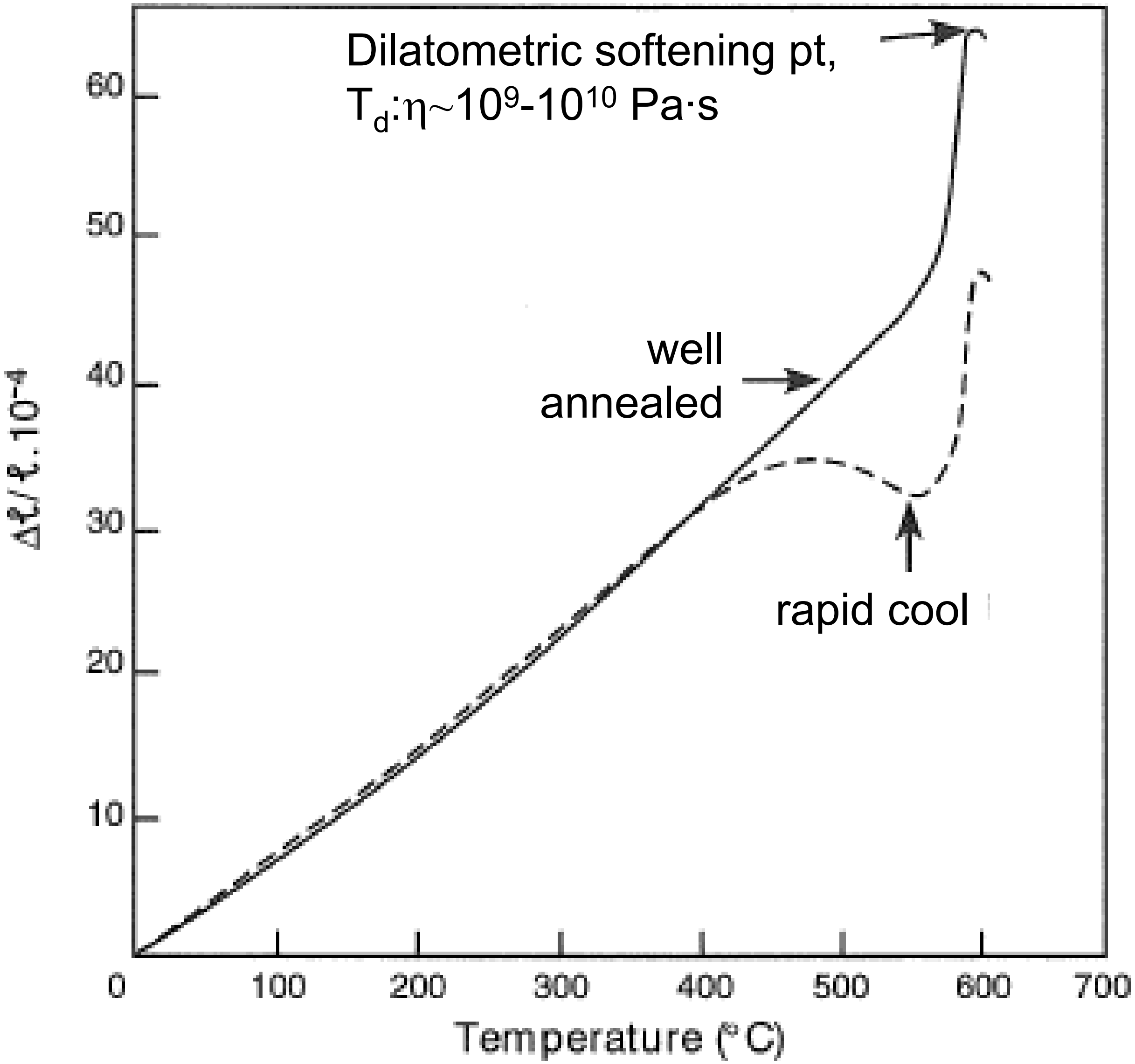

Figure 10-2. Effect of the cooling rate history on the expansion of a glass.

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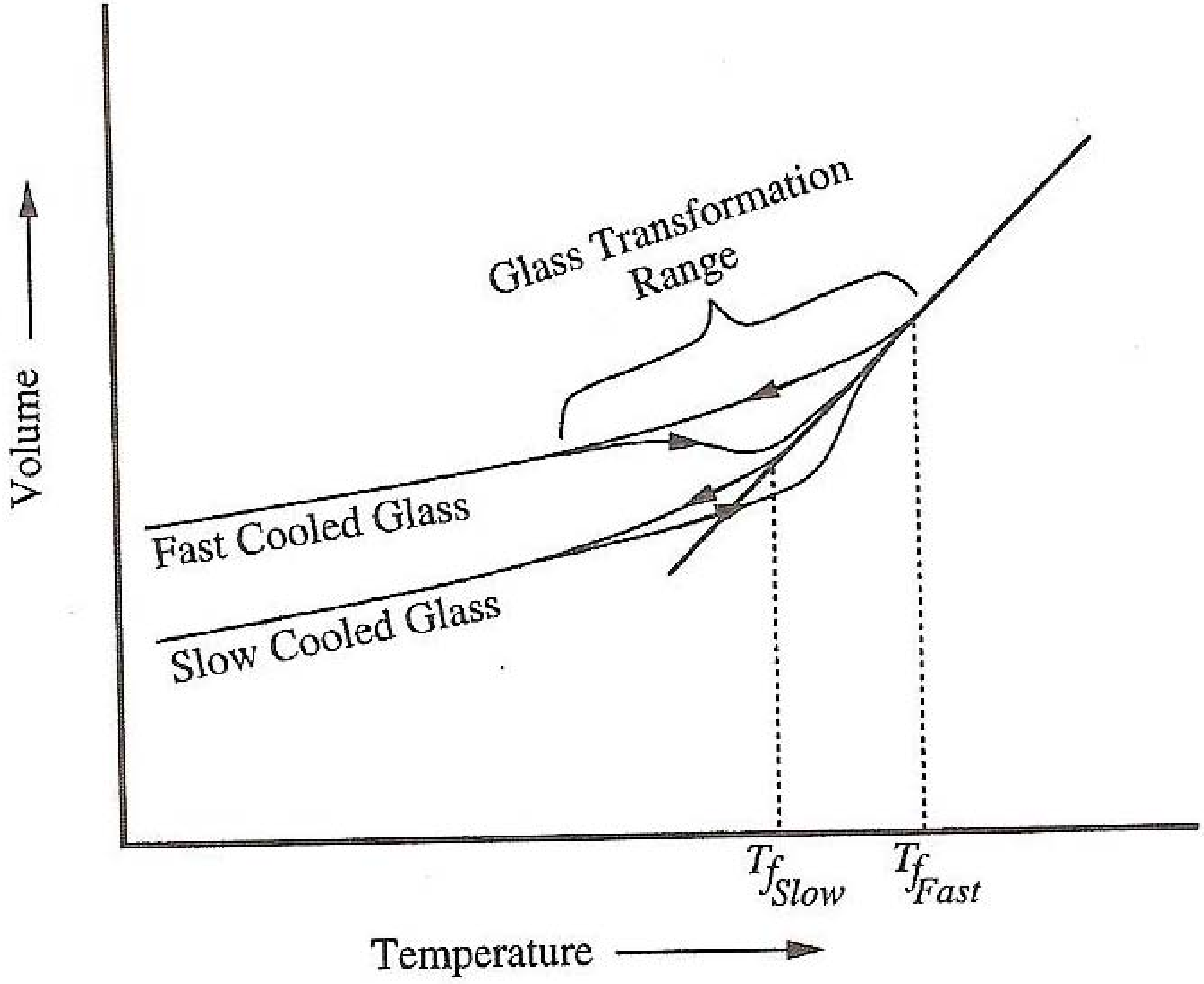
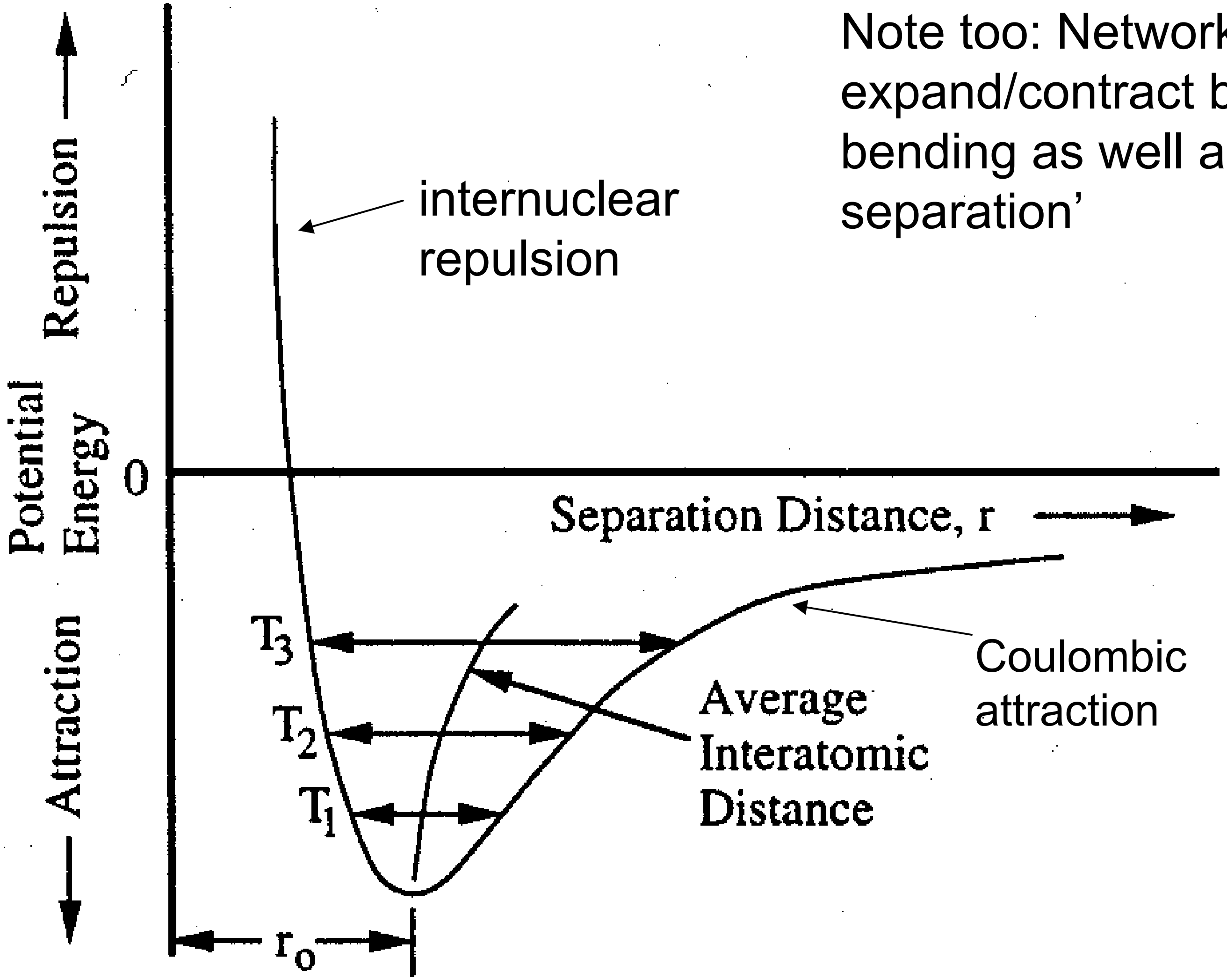


Shelby, 1997

Figure 7.4 *Effect of temperature on the volume of glass forming melts*

Note too: Networks can expand/contract by bond-bending as well as ‘bond-separation’



Shelby

Figure 7.7 *Condon–Morse cuve illustrating the cause of the thermal expansion of bonds*

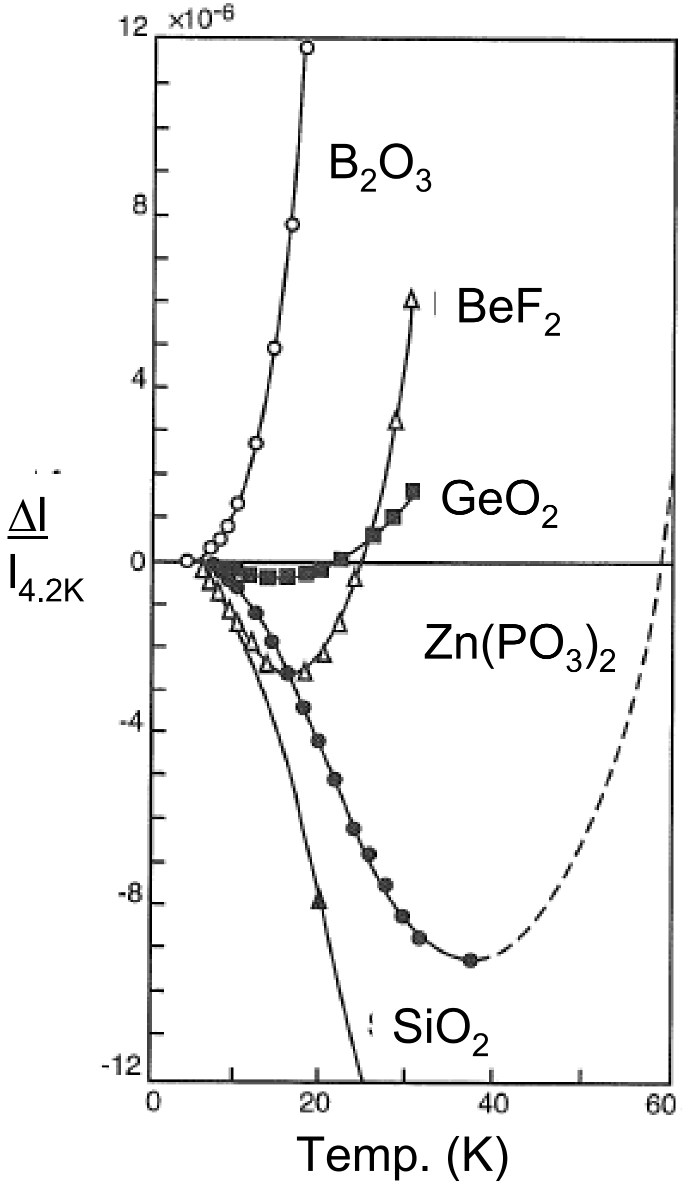


Figure 10-3. Thermal expansion curves of some single component glasses at low temperatures. (After J. T. Krause and C. R. Kurkjian, *J. Am. Ceram. Soc.*, **51**, 226 (1968).)

Note: Tetrahedral framework glasses exhibit 'anomalous' CTE behavior at low temperatures-

Tetrahedral rotations and bond angle changes

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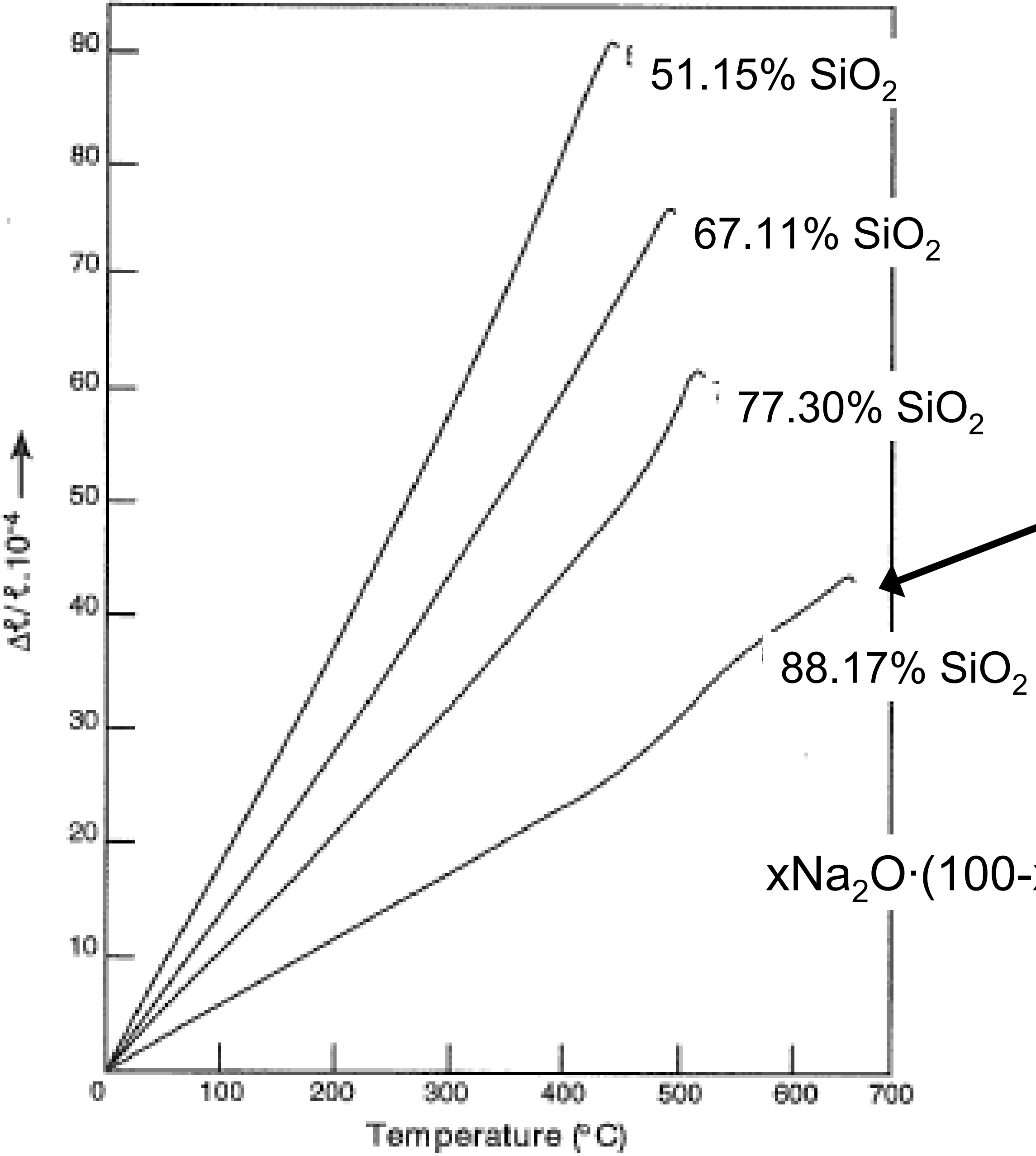
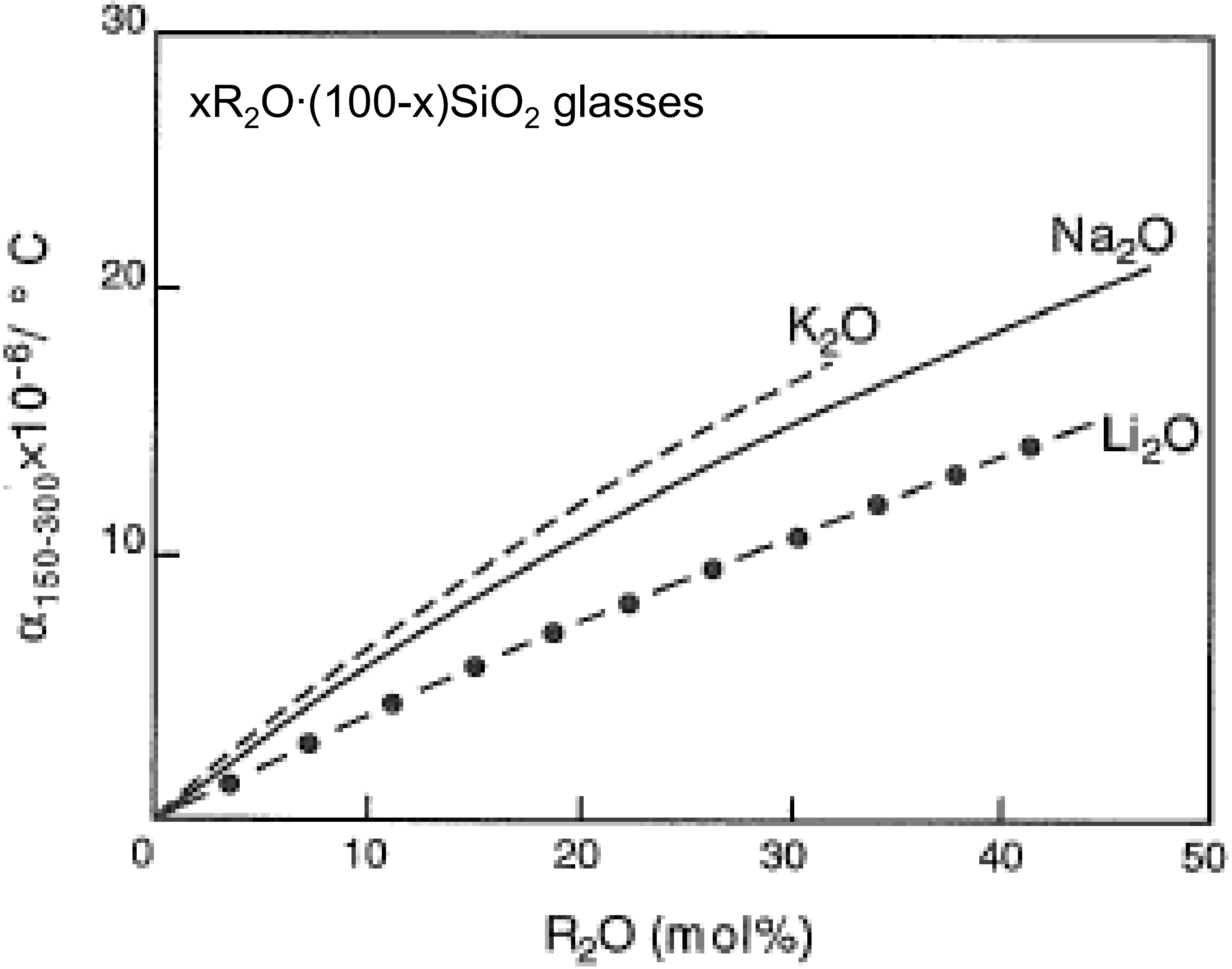


What accounts for this unusual CTE behavior?

$xNa_2O\cdot(100\text{-}x)SiO_2$ glasses

Reducing ‘network polymerization’ usually increases CTE



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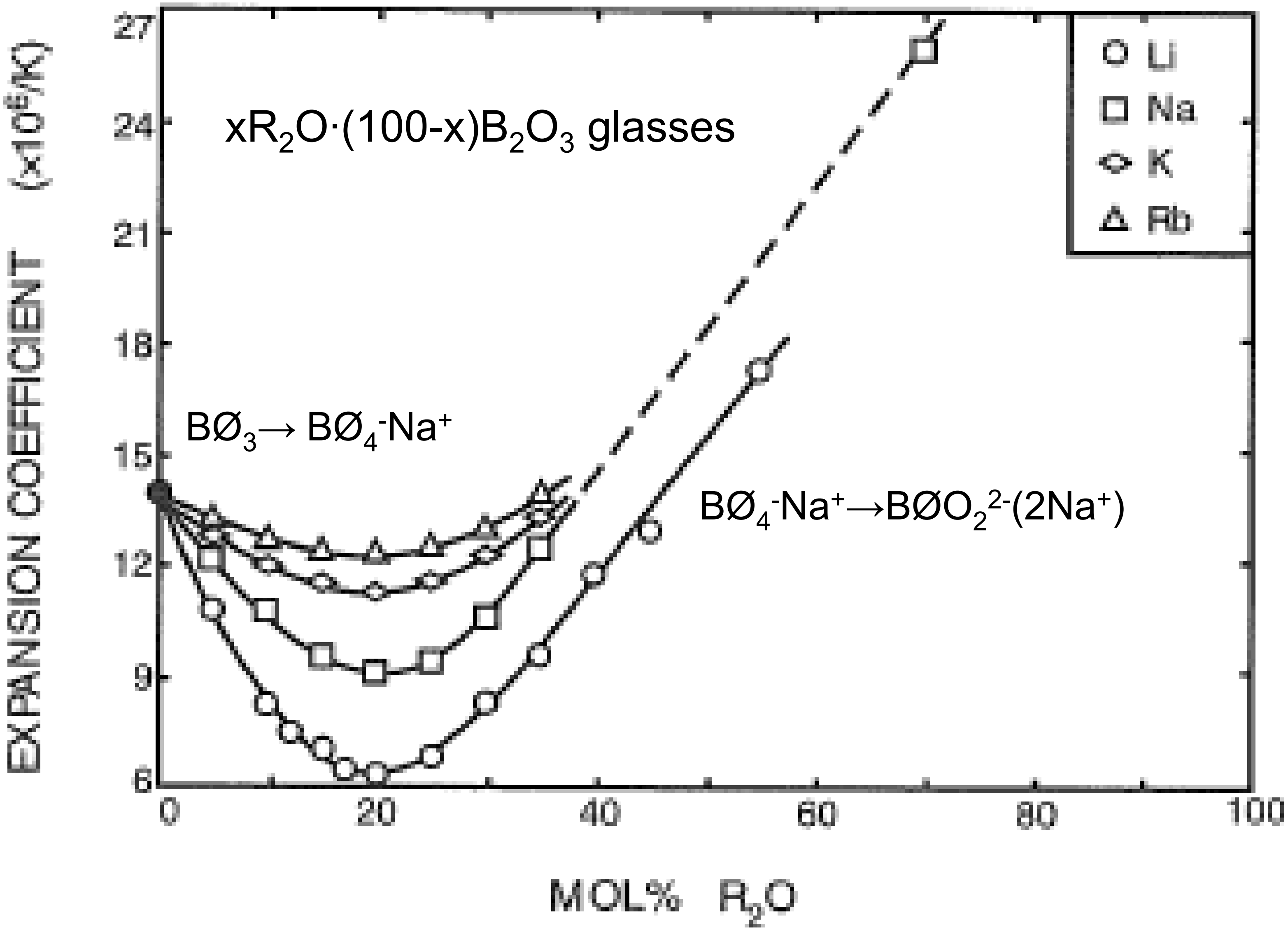
The ‘borate anomaly is evident in CTE data for borate glasses



$xR_2O\cdot(100-x)B_2O_3$ glasses

$BØ_3 \rightarrow BØ_4^-Na^+$

$BØ_4^-Na^+ \rightarrow BØO_2^{2-}(2Na^+)$

FS08

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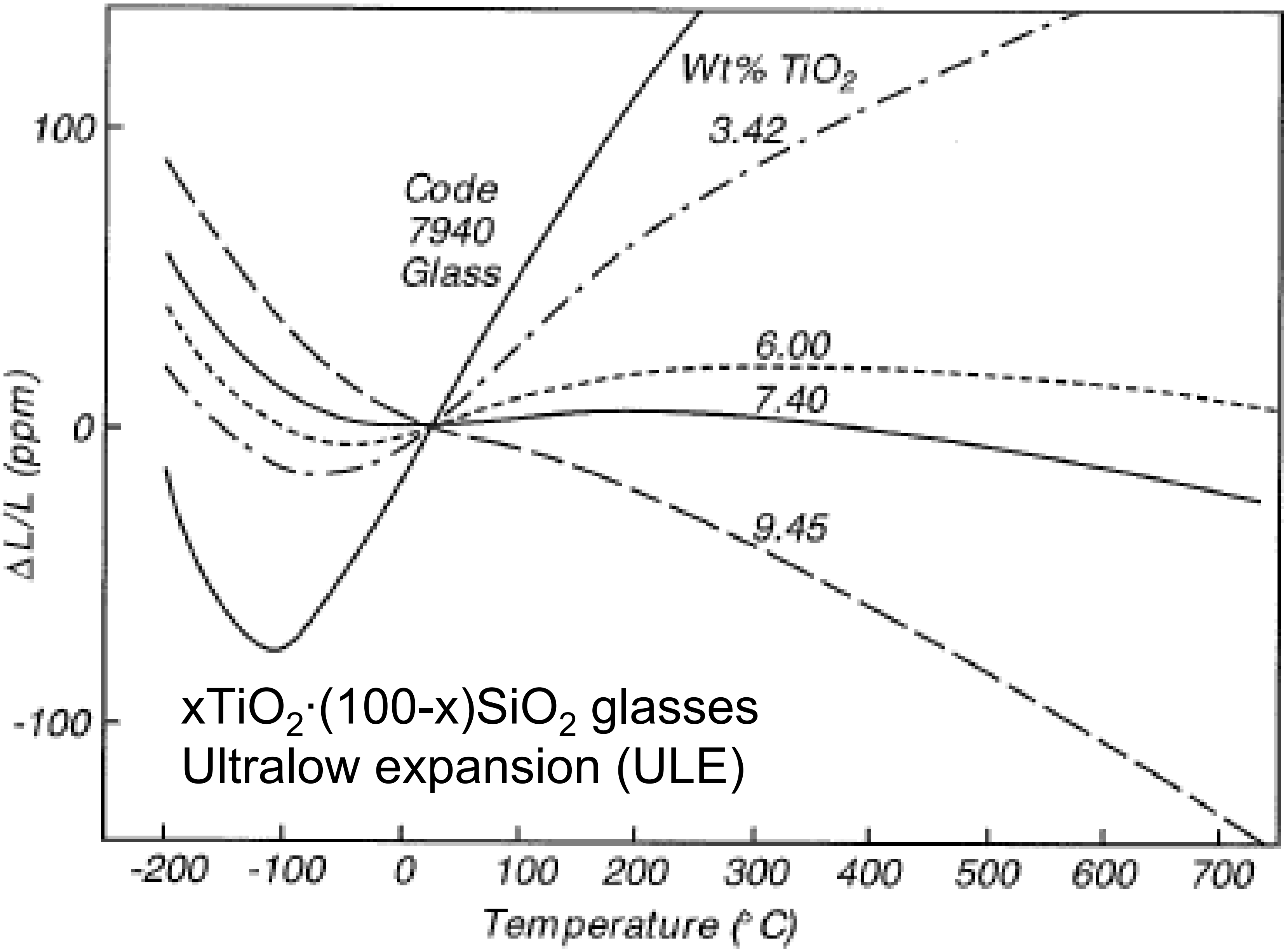

$xTiO_2{\cdot}(100\text{-}x)SiO_2$ glasses
Ultralow expansion (ULE)

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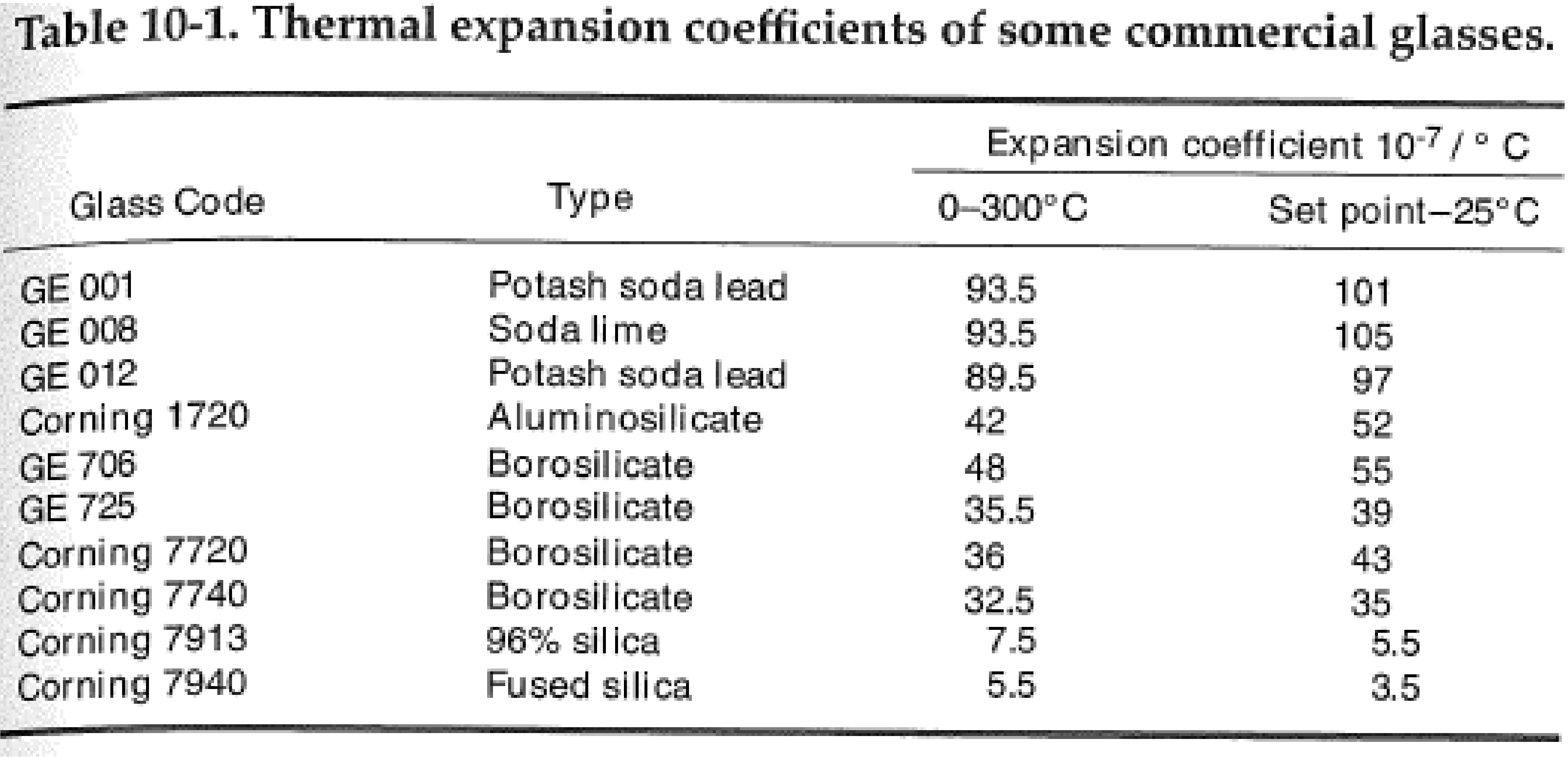
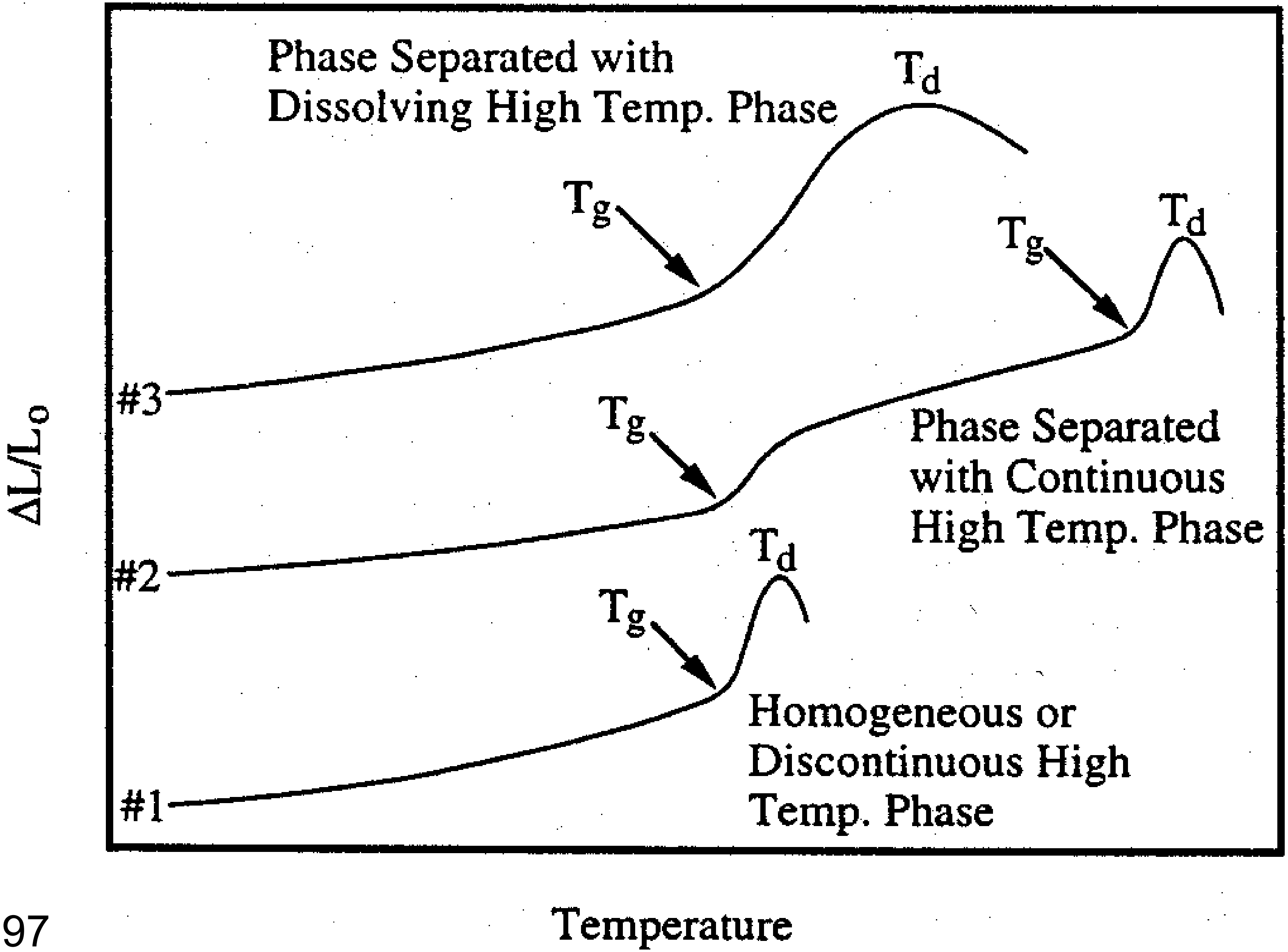


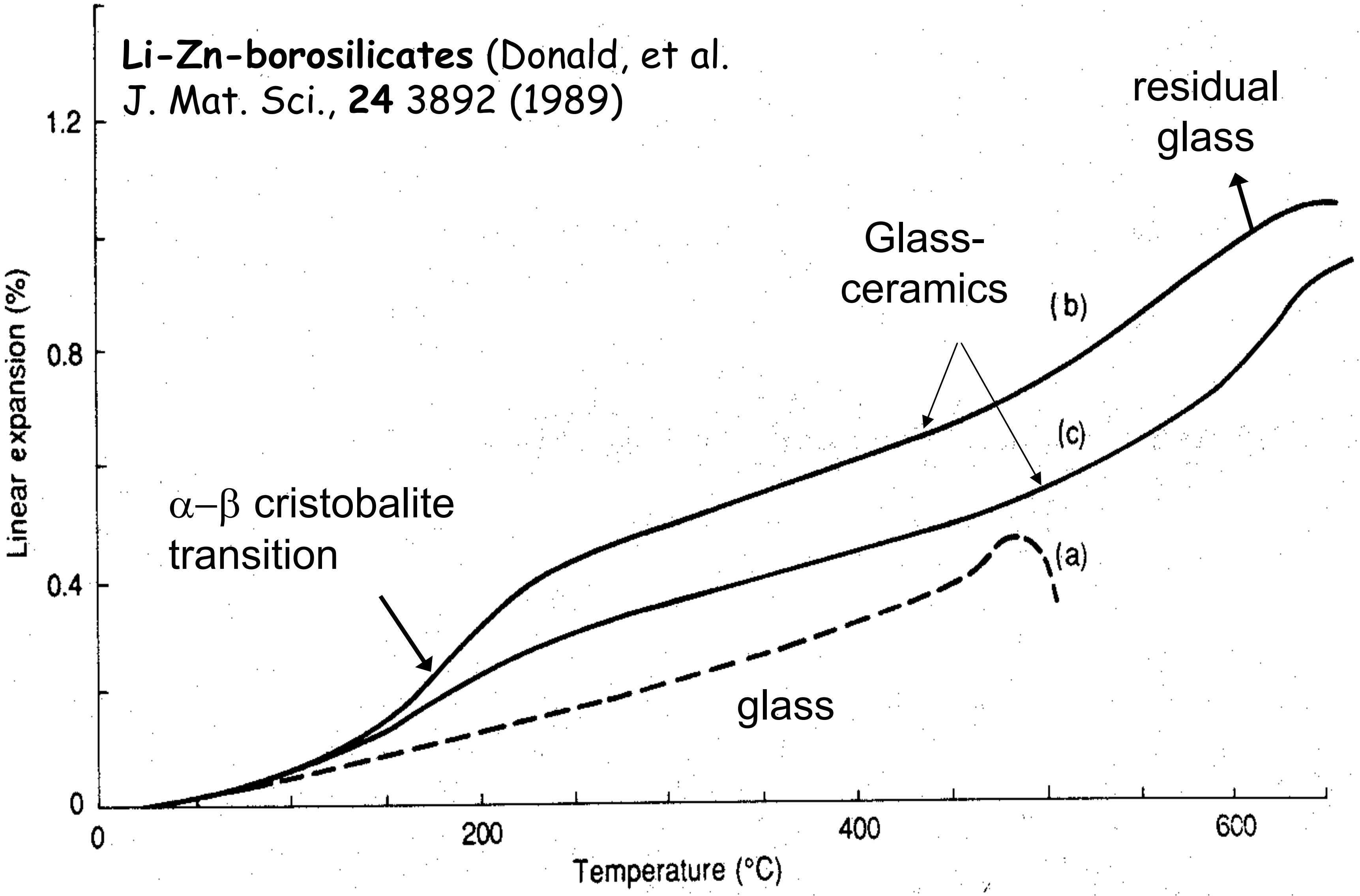
Table 10-1. Thermal expansion coefficients of some commercial glasses.

Glass Code	Type	Expansion coefficient 10^{-7} / ° C 0–300°C	 Set point–25°C
GE 001	Potash soda lead	93.5	101
GE 008	Soda lime	93.5	105
GE 012	Potash soda lead	89.5	97
Corning 1720	Aluminosilicate	42	52
GE 706	Borosilicate	48	55
GE 725	Borosilicate	35.5	39
Corning 7720	Borosilicate	36	43
Corning 7740	Borosilicate	32.5	35
Corning 7913	96% silica	7.5	5.5
Corning 7940	Fused silica	5.5	3.5



Shelby 1997

Figure 7.11 *Effect of phase separation on the thermal expansion curves of glasses*



Li-Zn-borosilicates (Donald, et al. J. Mat. Sci., **24** 3892 (1989)

residual glass

Glass-ceramics

α–β cristobalite transition

glass

Brief CTE Case Study: Li-aluminosilicate glass-ceramics

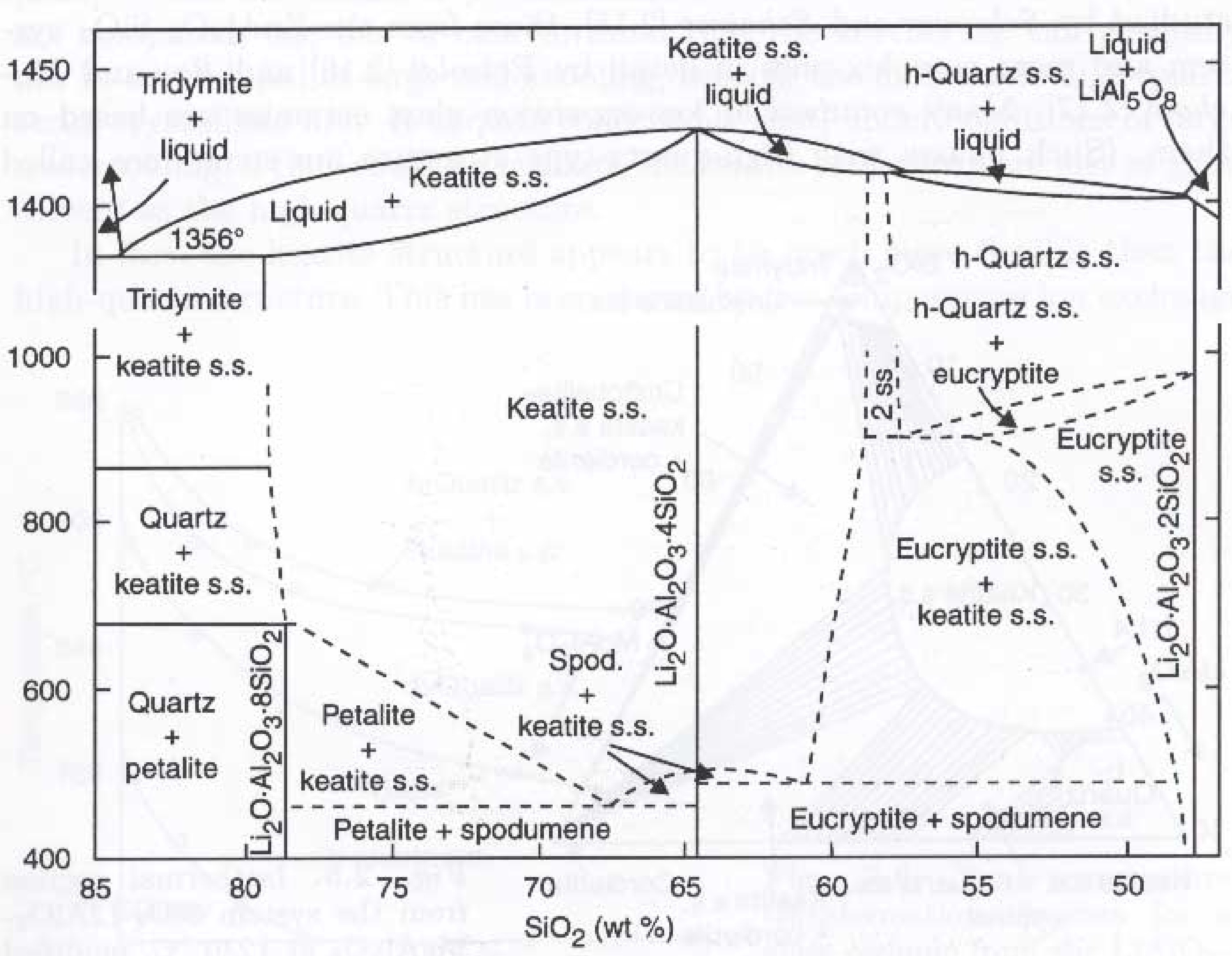


Fig. 2.4. System $Li_2O{\cdot}Al_2O_3{\cdot}2SiO_2$-$SiO_2$, after [2.13]

$Li_2O-Al_2O_3-nSiO_2$: β-spodumene/β-quartz solid solutions

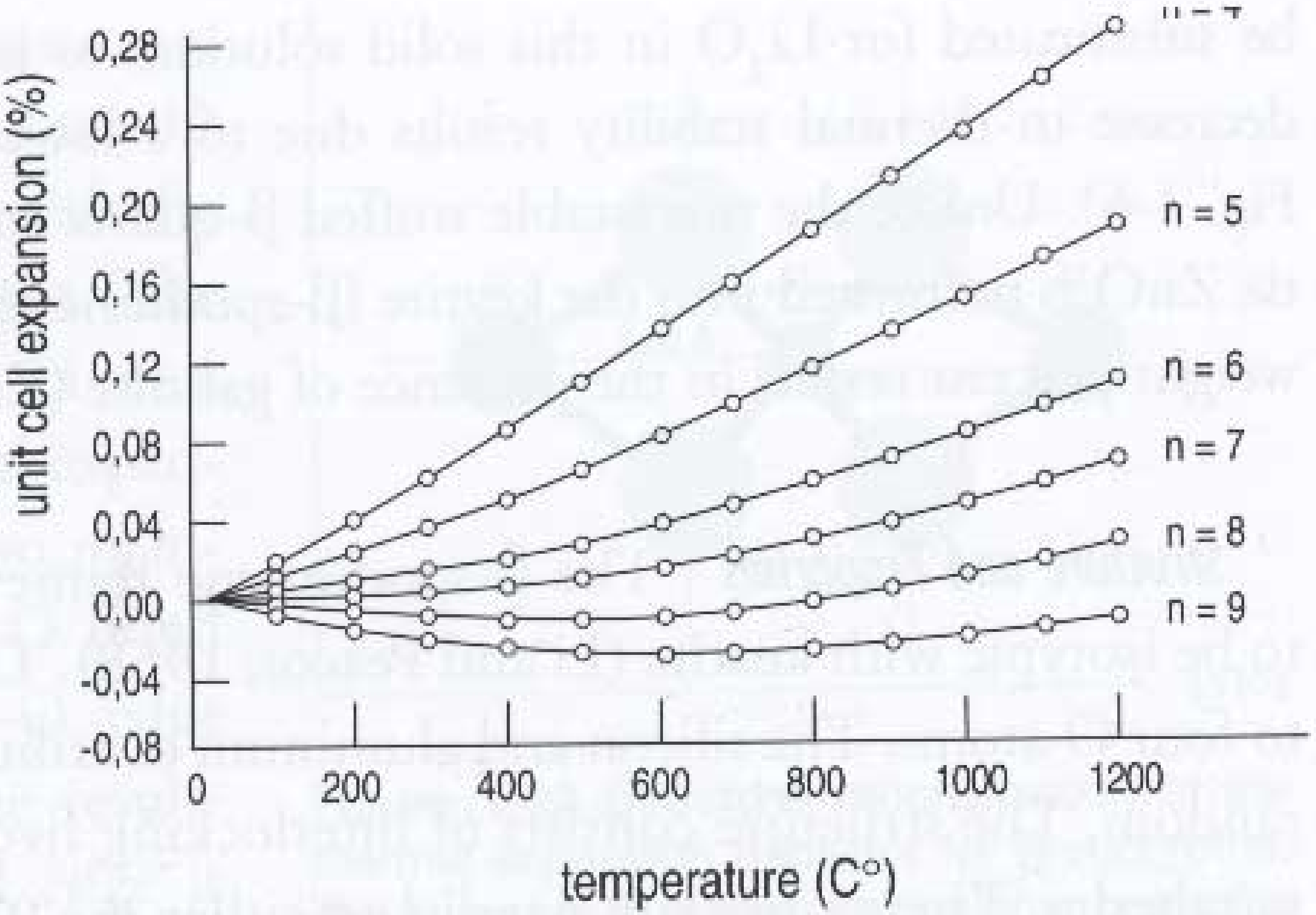
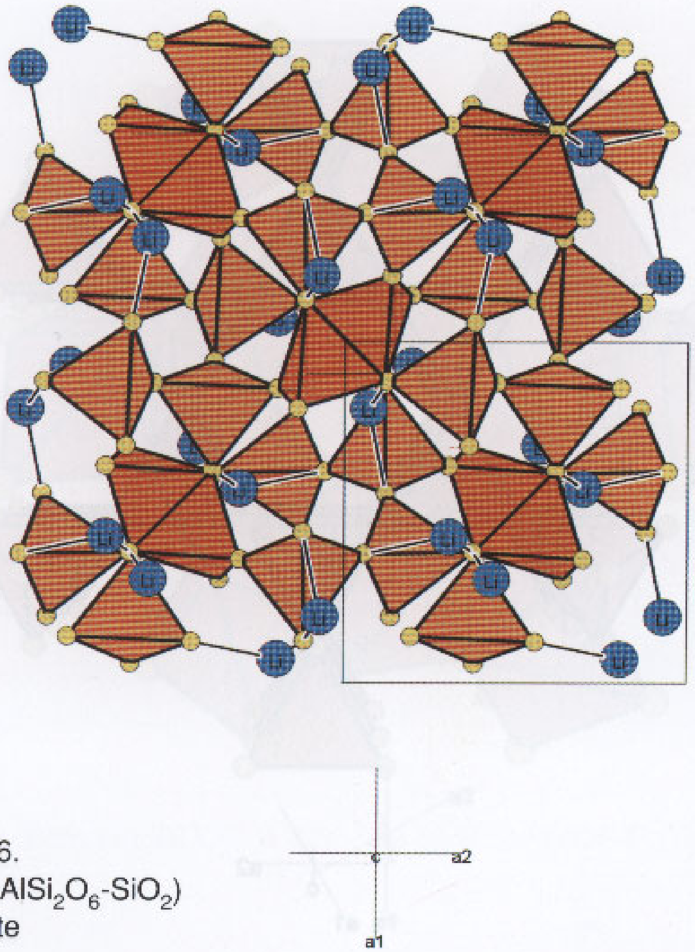
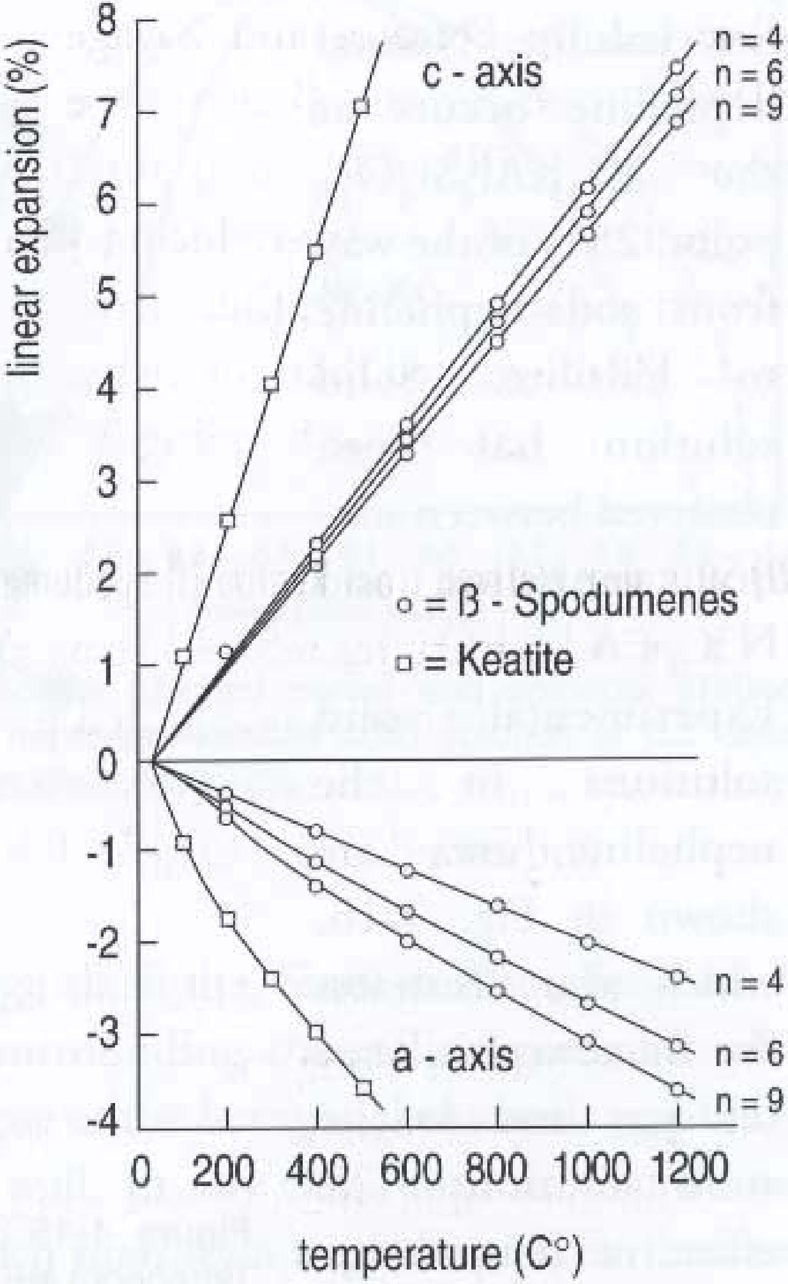


Figure 1-14 Volume thermal expansion in crystals of $Li_2O\cdot Al_2O_3\cdot nSiO_2$ β-spodumene solid solution (after Ostertag et al., 1968).

Low thermal expansion due to open tetrahedral crystalline networks



Appendix Figure 6.
β-Spodumene ($LiAlSi_2O_6$-SiO_2)
Framework Silicate



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From Beall, "Glass-Ceramics, in *Commercial Glasses* (Advances in Ceramics, **18)**, 1986

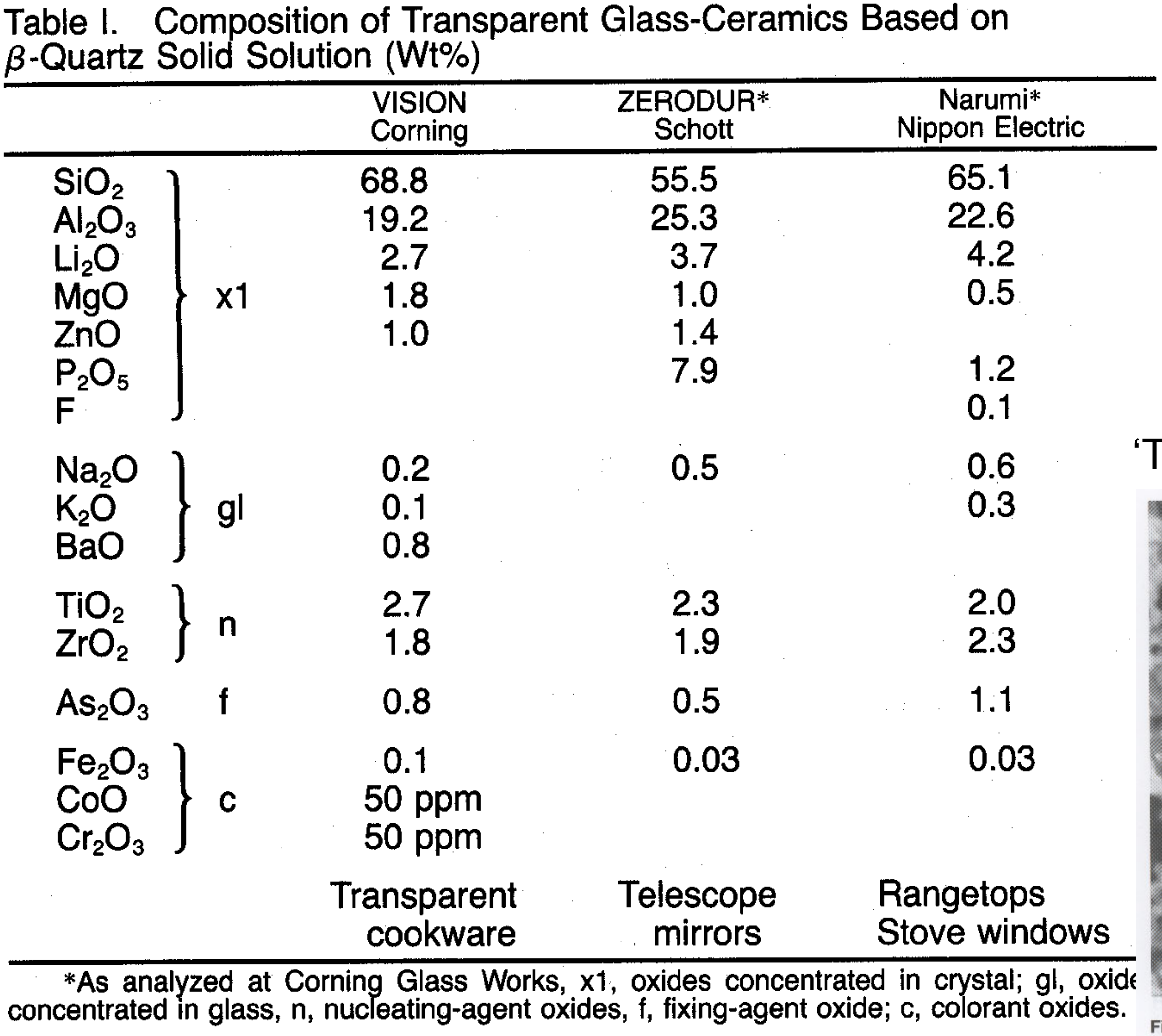


Table I. Composition of Transparent Glass-Ceramics Based on β-Quartz Solid Solution (Wt%)

		VISION Corning	ZERODUR* Schott	Narumi* Nippon Electric
SiO_2	x1	68.8	55.5	65.1
Al_2O_3		19.2	25.3	22.6
Li_2O		2.7	3.7	4.2
MgO		1.8	1.0	0.5
ZnO		1.0	1.4	
P_2O_5			7.9	1.2
F				0.1
Na_2O	gl	0.2	0.5	0.6
K_2O		0.1		0.3
BaO		0.8		
TiO_2	n	2.7	2.3	2.0
ZrO_2		1.8	1.9	2.3
As_2O_3	f	0.8	0.5	1.1
Fe_2O_3	c	0.1	0.03	0.03
CoO		50 ppm		
Cr_2O_3		50 ppm		
		Transparent cookware	Telescope mirrors	Rangetops Stove windows

*As analyzed at Corning Glass Works, x1, oxides concentrated in crystal; gl, oxide concentrated in glass, n, nucleating-agent oxides, f, fixing-agent oxide; c, colorant oxides.

'Corning ware': (1-2 μm)

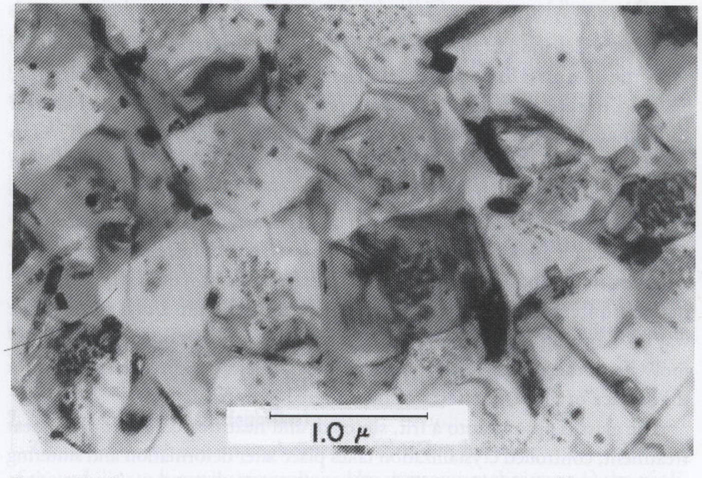


Figure 2-6 Microstructure of β-spodumene solid solution (Corning Ware®).

'Transparent' glass-ceramic (~0.1 μm)

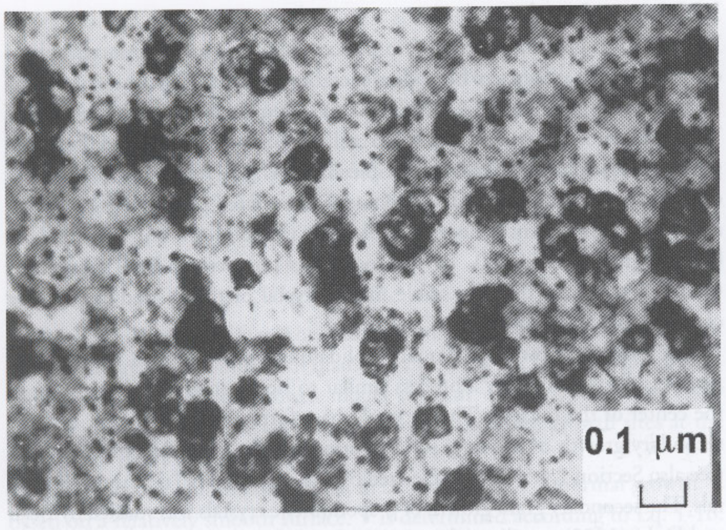
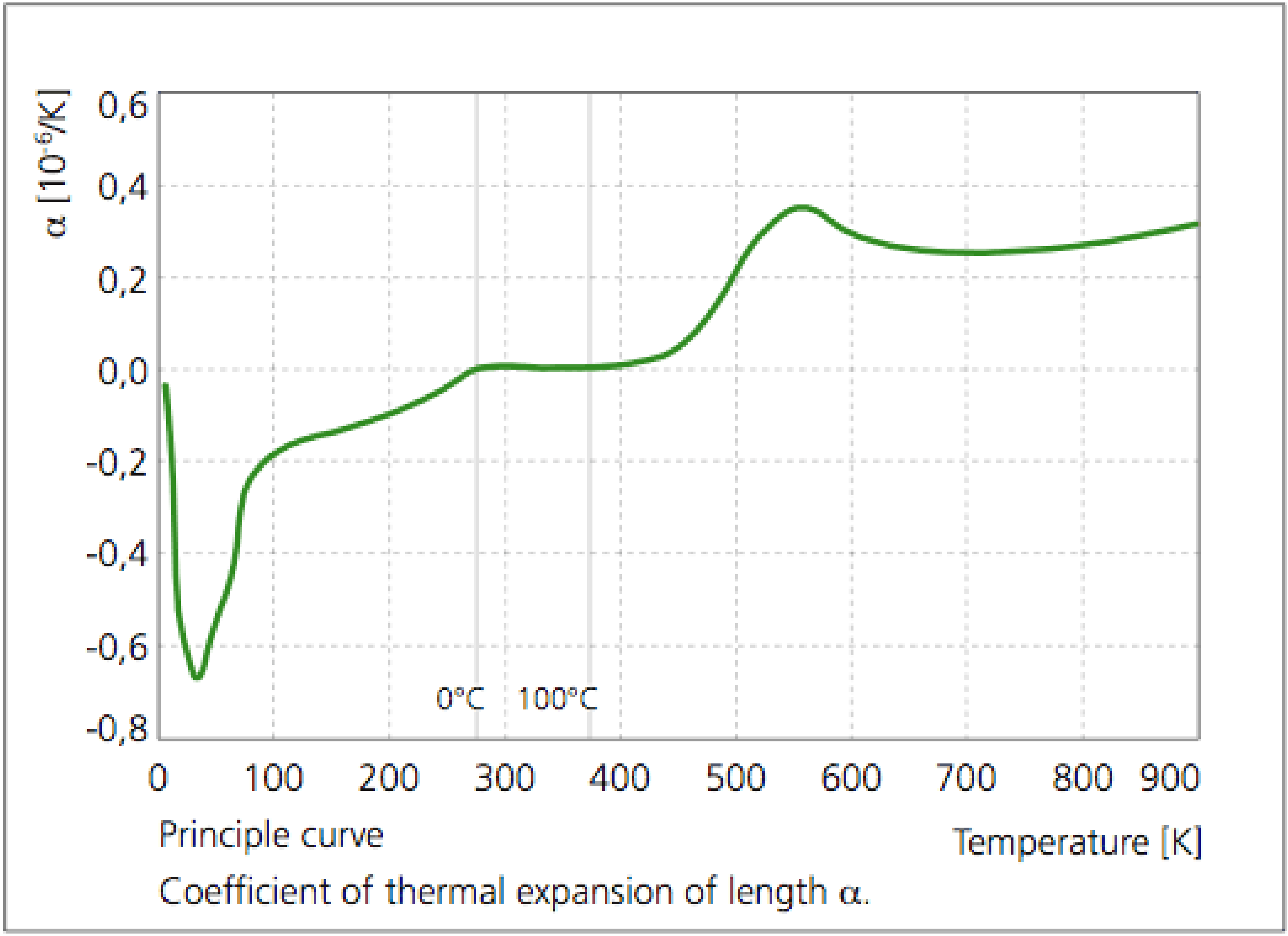


Figure 1-36 TEM image showing crystallized SiO_2–Al_2O_3–Li_2O–TiO_2 glass, heat treated to 950°C. β-quartz solid solution precipitated.

Zerodur- ultralow expansion glass-ceramics



http://www.pgo-online.com/intl/katalog/curves/zerodur_dkurve.html

8-m mirror blank (45-tons of glass, melted at 1700 K)- Schott/Mainz

http://grus.berkeley.edu/~jrg/MATERIALS/node9.html

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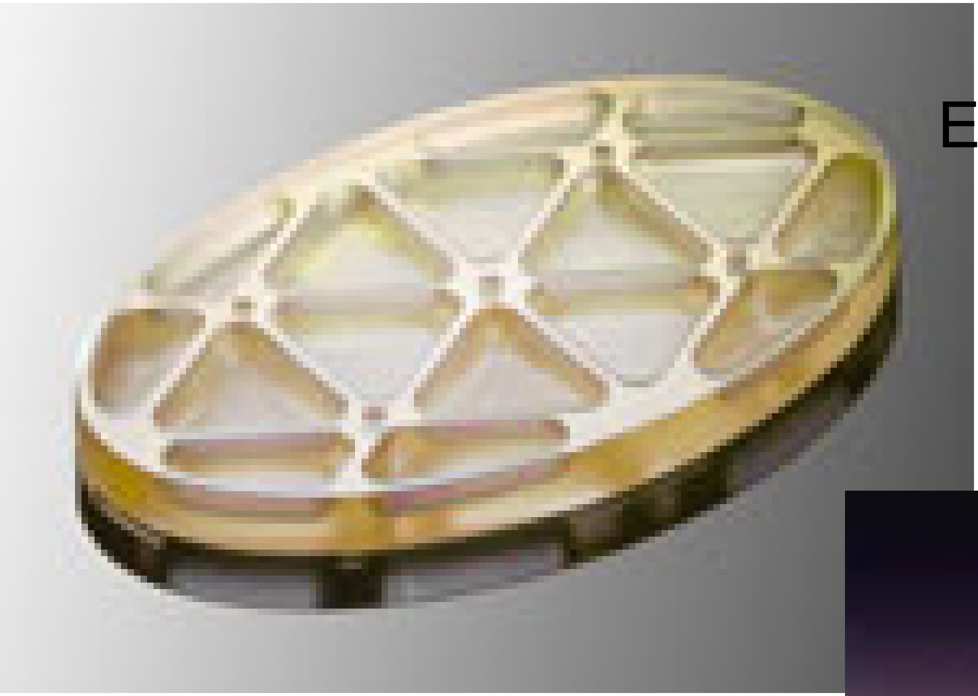
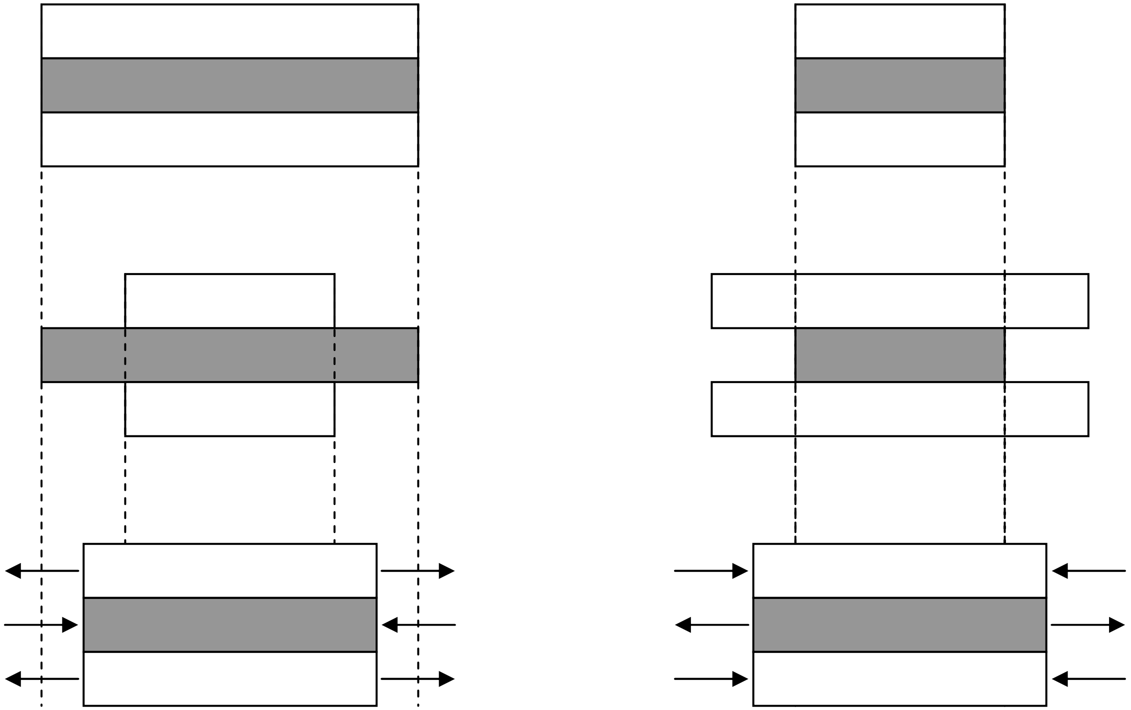


European Southern Observatory 'Very Large Telescope' Paranol, Chile

Thermal Shock: T<T_g (no relaxation)



Quench Hot-to-Cold
(cold surface, hot center)
Surface in Tension

Rapid Heat: Cold-to-Hot
(hot surface, cold center)
Surface Compression

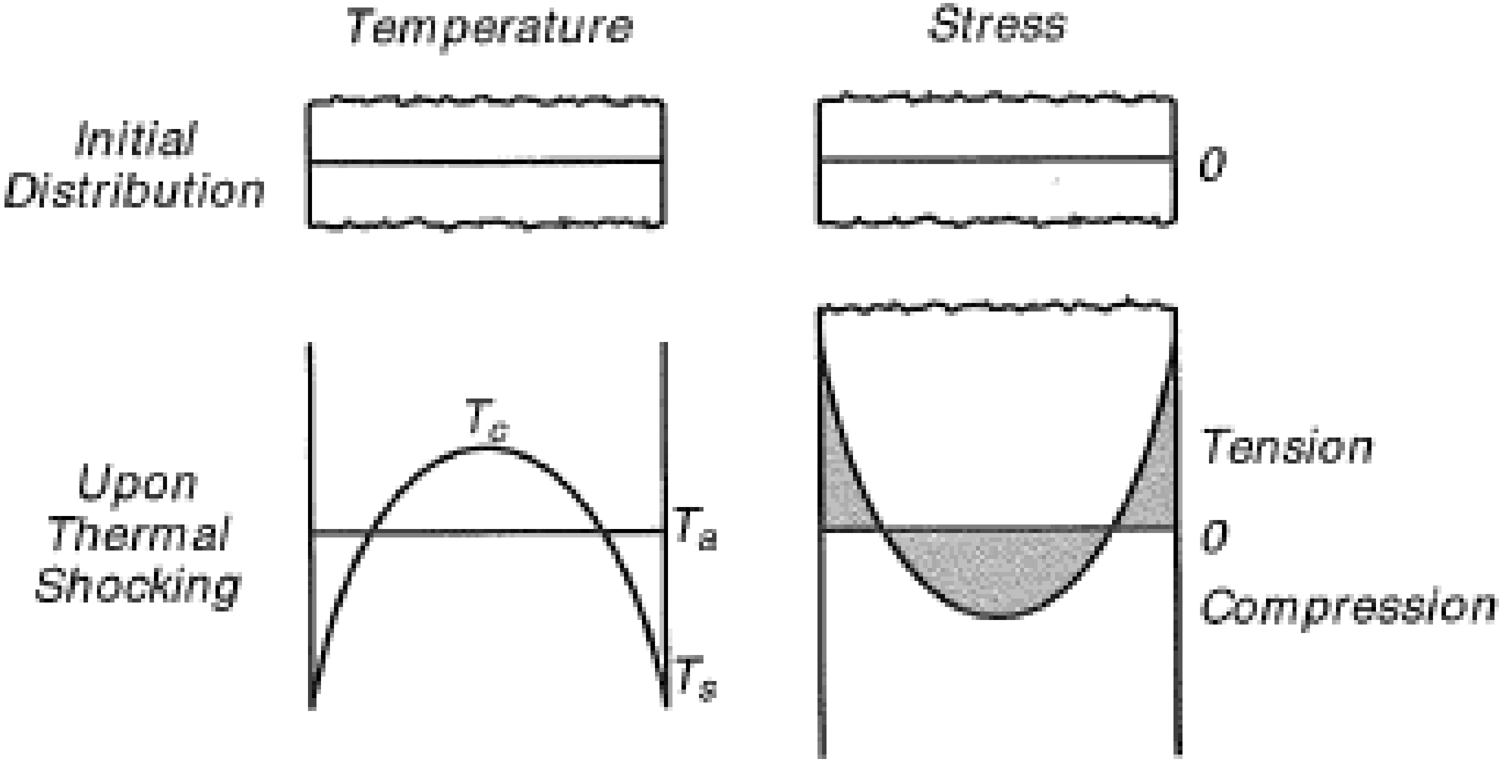


Figure 10-8. Stress production in glass due to thermal shock.

For a plate cooled symmetrically at Φ°C/s, the planar stresses are given by

$$\sigma_x = [E/3(1-\nu)]\Phi L^2\alpha(\rho\cdot C_p/K)$$

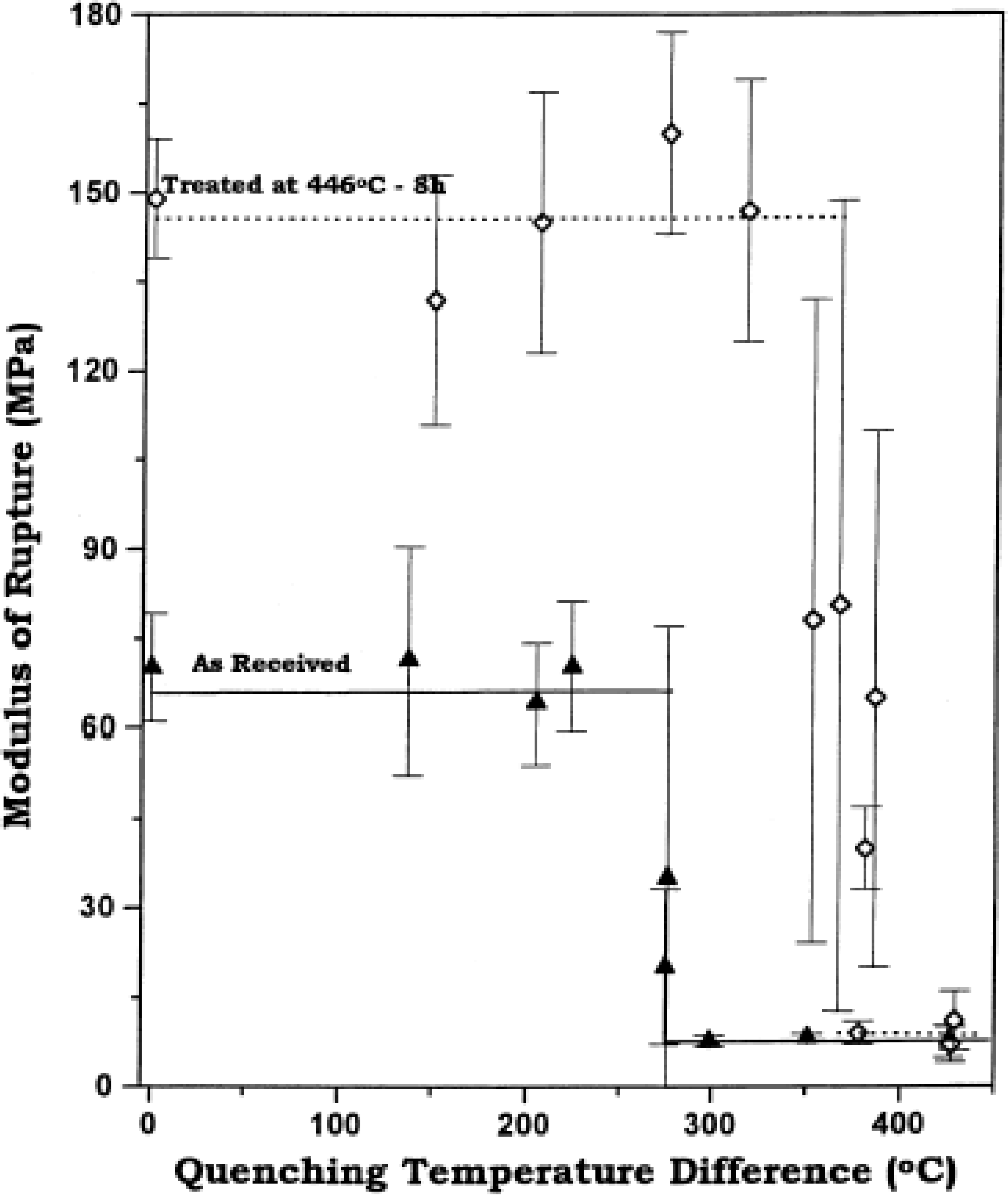
where L is the half-thickness of the plate, ρ is density, C_p is heat capacity and K is thermal conductivity; E is elastic modulus and ν is the Poisson's ratio.

Thermal Shock

Thermal Shock Resistance:

$\Delta T = m[\sigma_f/\alpha \cdot E][K/\rho \cdot C_p]^{1/2}$

Where m is a constant and σ_f is the tensile strength.



PEITL, O. & ZANOTTO, E. D. "*Thermal Shock Properties of Chemically Toughened Borosilicate Glass*". J. Non-Cryst. Solids v. 247/1-3 (1999) 39-49

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Heat Capacity

Heat Capacity (C)

- Amount of heat (Q) required to change the temperature by one degree of a fixed amount of material
- Units for C: calories/(g·°C), calories/(mole·°C), Joules/(kg·°C), Joules/(mole·°C); recall that 1 cal=4.18 J
  - C_p (constant pressure), C_v (constant volume)
- Specific Heat: (C-material)/(C-water at 15°C), although sometimes defined as ‘heat capacity per g material’
- Solids: C depends on phonon vibrations
  Liquids: contributions from configurational entropy
- Typically measured by differential scanning calorimetry
- At room temperature, there is little compositional dependence for $C_p \sim 900\ J \cdot kg^{-1} \cdot K^{-1}$

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Heat capacity increases monotonically above T_g- related to structural rearrangements in the supercooled liquid (configurational heat capacity)

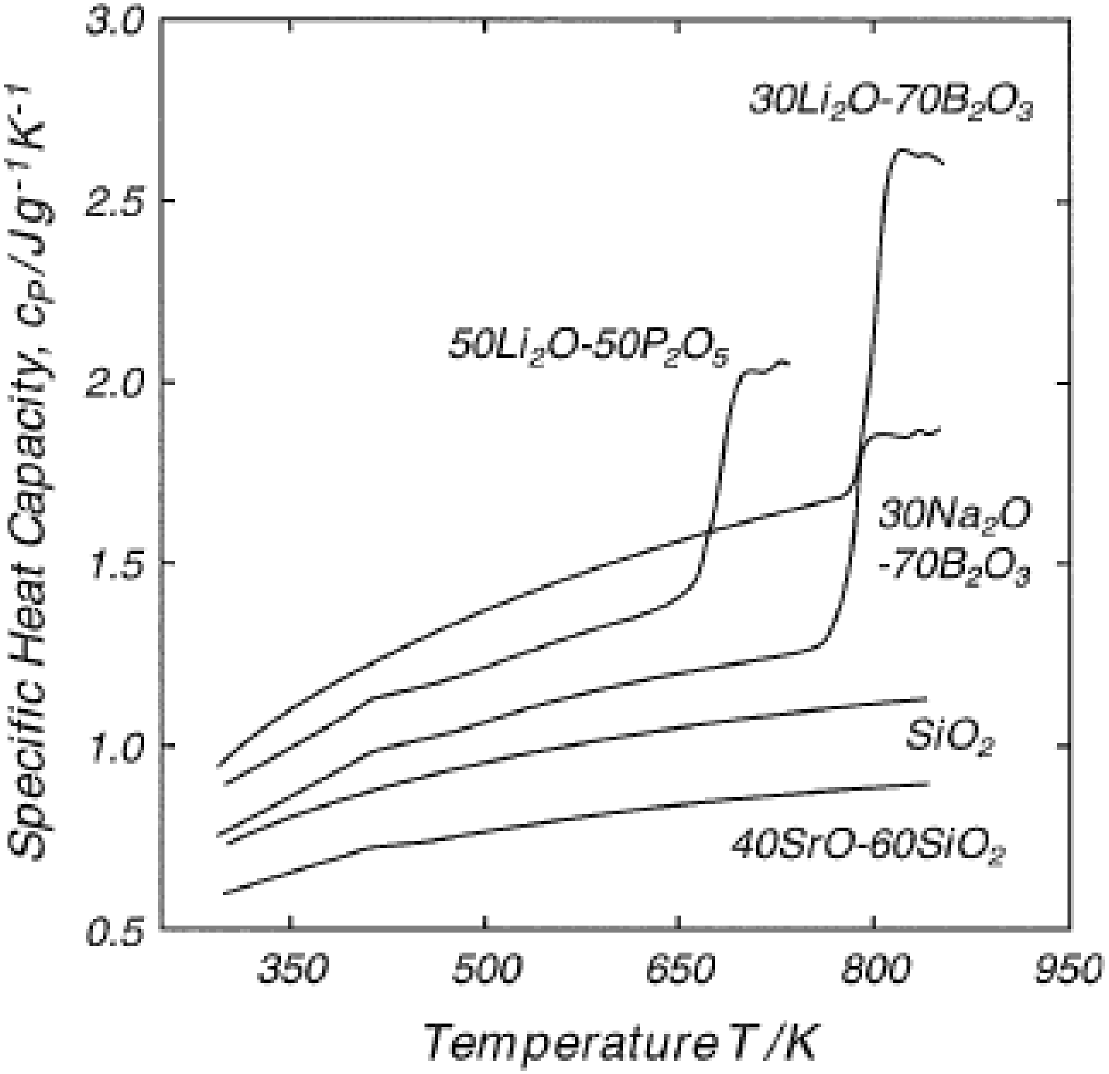

Figure 11-1. Heat capacity of some oxide glasses. (After Inaba *et al*[(3)].)

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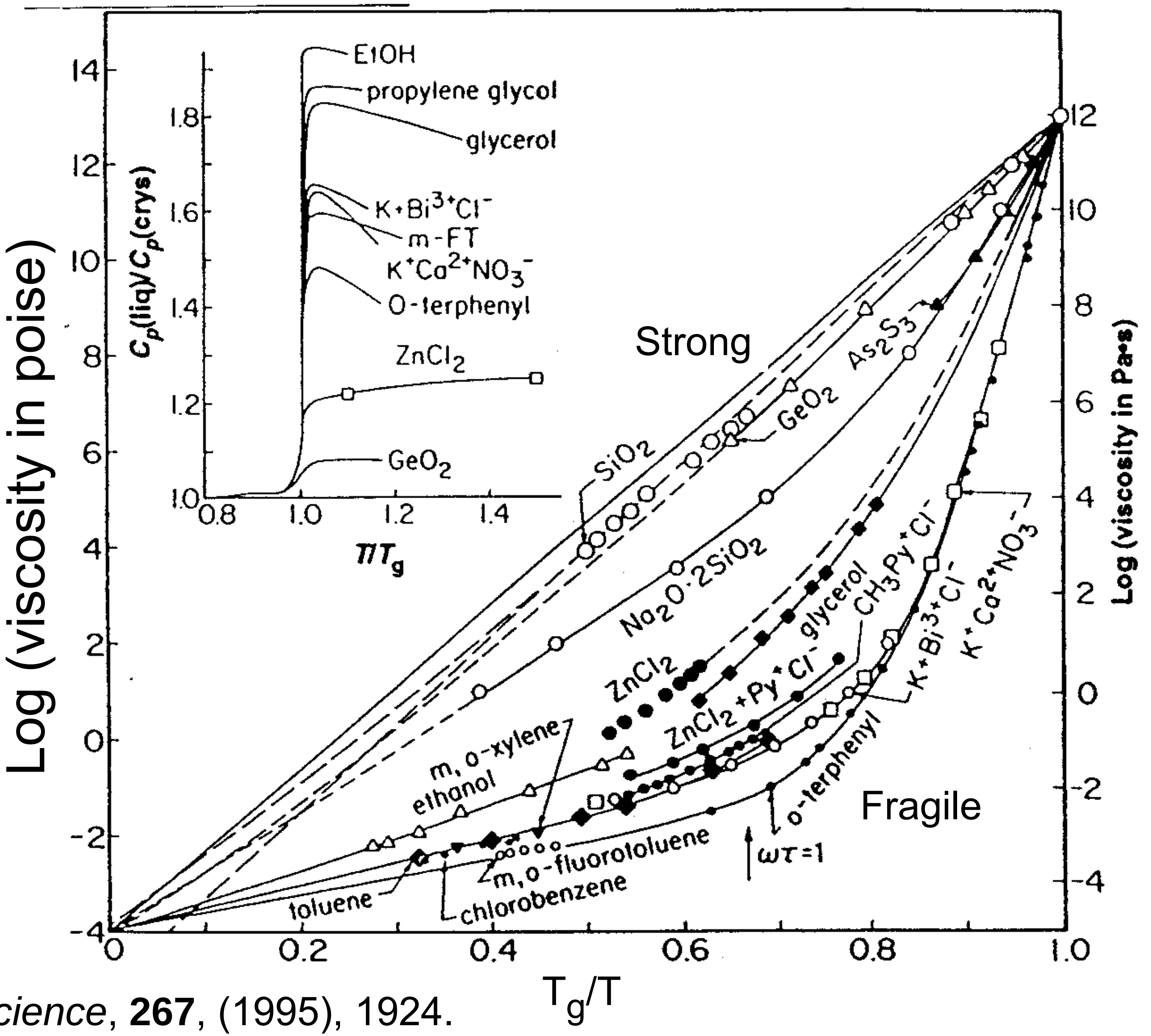
Melt Fragility



From C. A. Angell, *Science*, **267**, (1995), 1924.

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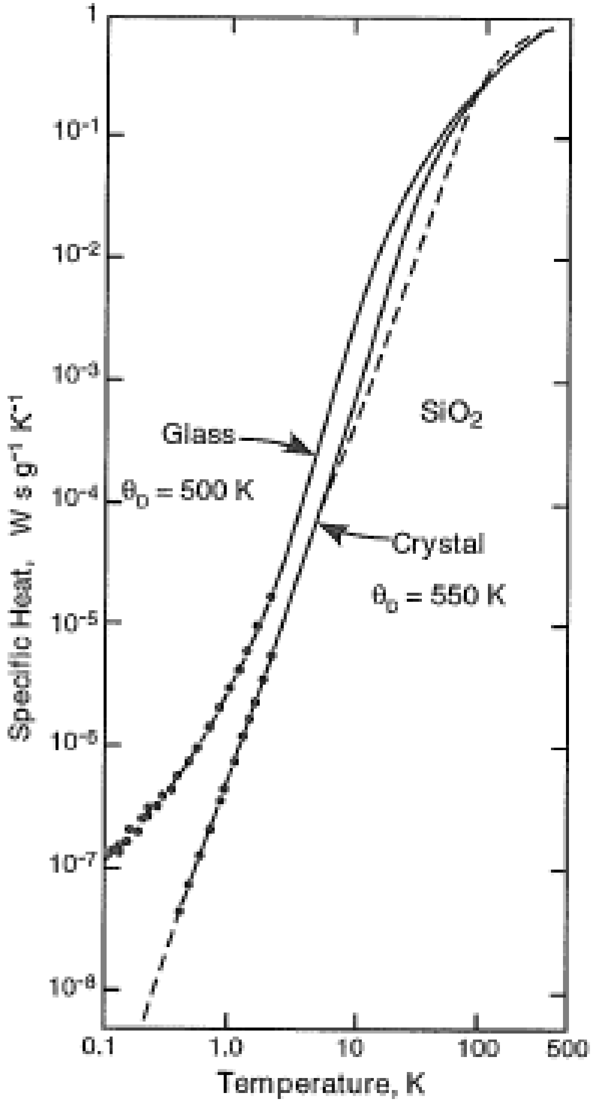

Figure 11-2. Heat capacity of vitreous silica and α-quartz at low temperatures. θ_D=Debye temperature. (After Pohl$^{(5)}$. Reproduced with permission of Springer-Verlag.)

At low temperatures, heat capacity of electrical insulators described by the Debye relationship (θ_D is Debye Temp):

$$C_v = \frac{12\pi^4}{5} N k_B \left(T/\theta_D\right)^3$$

$$\theta_D = (\hbar / k_B)[6\pi^2 \nu_D^3 N / V]^{1/3}$$

where ν_D is related to the vibrational (phonon) energies of the chemical bonds.

Glasses do not follow the Debye relationship and appear to have 'excess' heat capacity as T → 0 K.

- glasses have additional low frequency vibrational modes, including the 'Boson peak'

Thermal Conductivity

Heat Transfer in Glasses & Melts

- Up to 300°C: **Conduction** dominates
- Above 300°C: **Conduction** and **Radiation**
- Above 800°C: **Radiation** and **Convection**, conduction is less important

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Thermal conductivity (K) defined by Fourier's Law:

Heat flux = -(thermal conductivity) x (temperature gradient)

Φ (watts/m^2) = -K_c (watts/m·K) x dT/dx (K/m)

Temperature	K_c (w/m·K)
20°C	1.0
600°C	1.5
1200°C	2.0

Phonon excitation mechanism

- low conductivity compared to crystals
- Little dependence on composition

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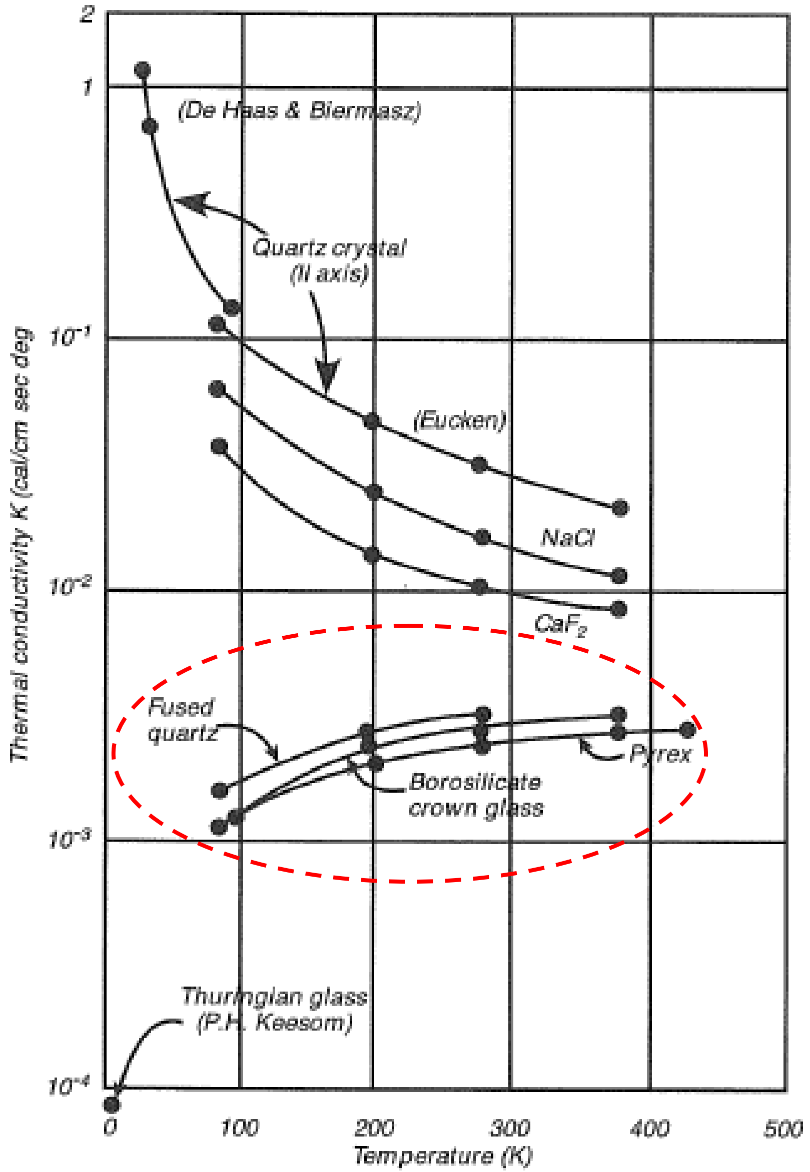


Figure 12-2. Temperature dependence of the phonon thermal conductivity of various glasses and crystals. (After C. Kittel(11), Fig. 2 p231. Elsevier Science Publishers. 1971. Reproduced with permission the publishers).

Phonon-mediated thermal conductivity of glass is (relatively) independent of composition…

- K increases with temperature (for glasses) because of an increase in heat capacity….

Radiative conductivity

(K_R): energy transfer by photons

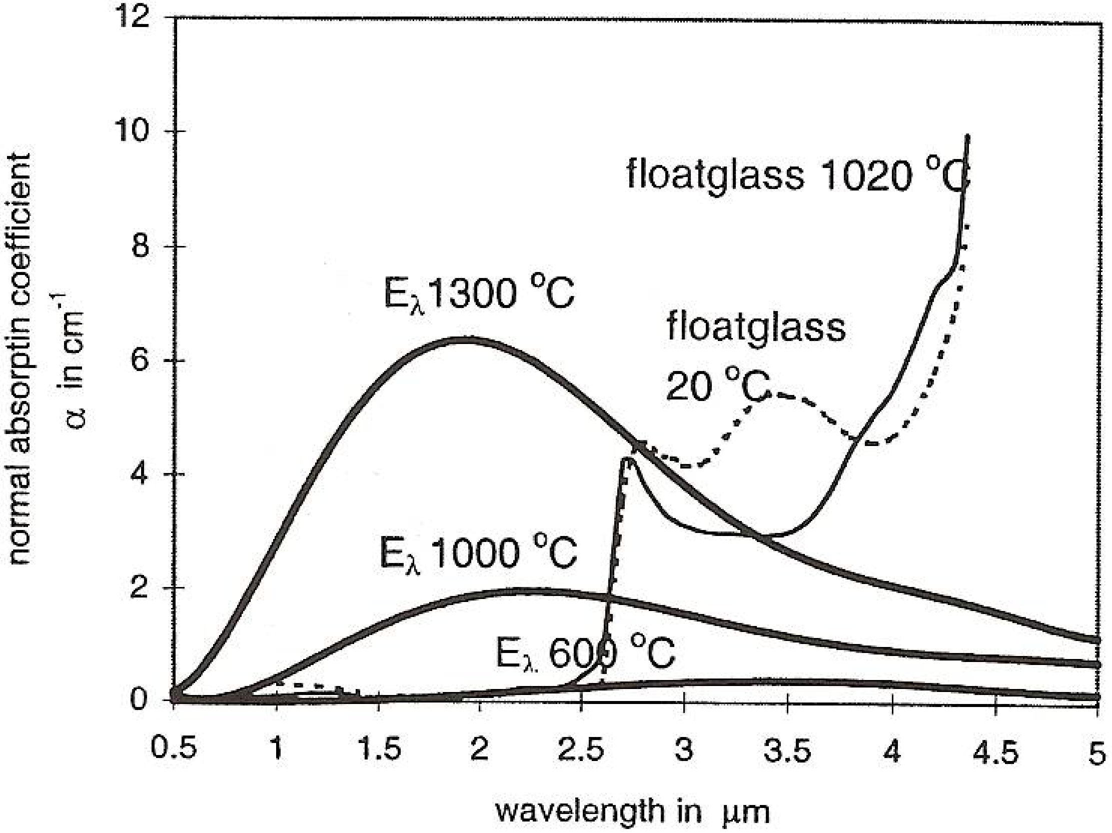


Figure 13 Spectrum of heat radiation of a black body at 3 spectral absorption of float-glass

Below 600°C: blackbody radiation at wavelengths (>2.5µm) where glass absorbs; heat must conduct by phonons

Above 1000°C: Blackbody radiation is transmitted by glass- heat conducts radiatively

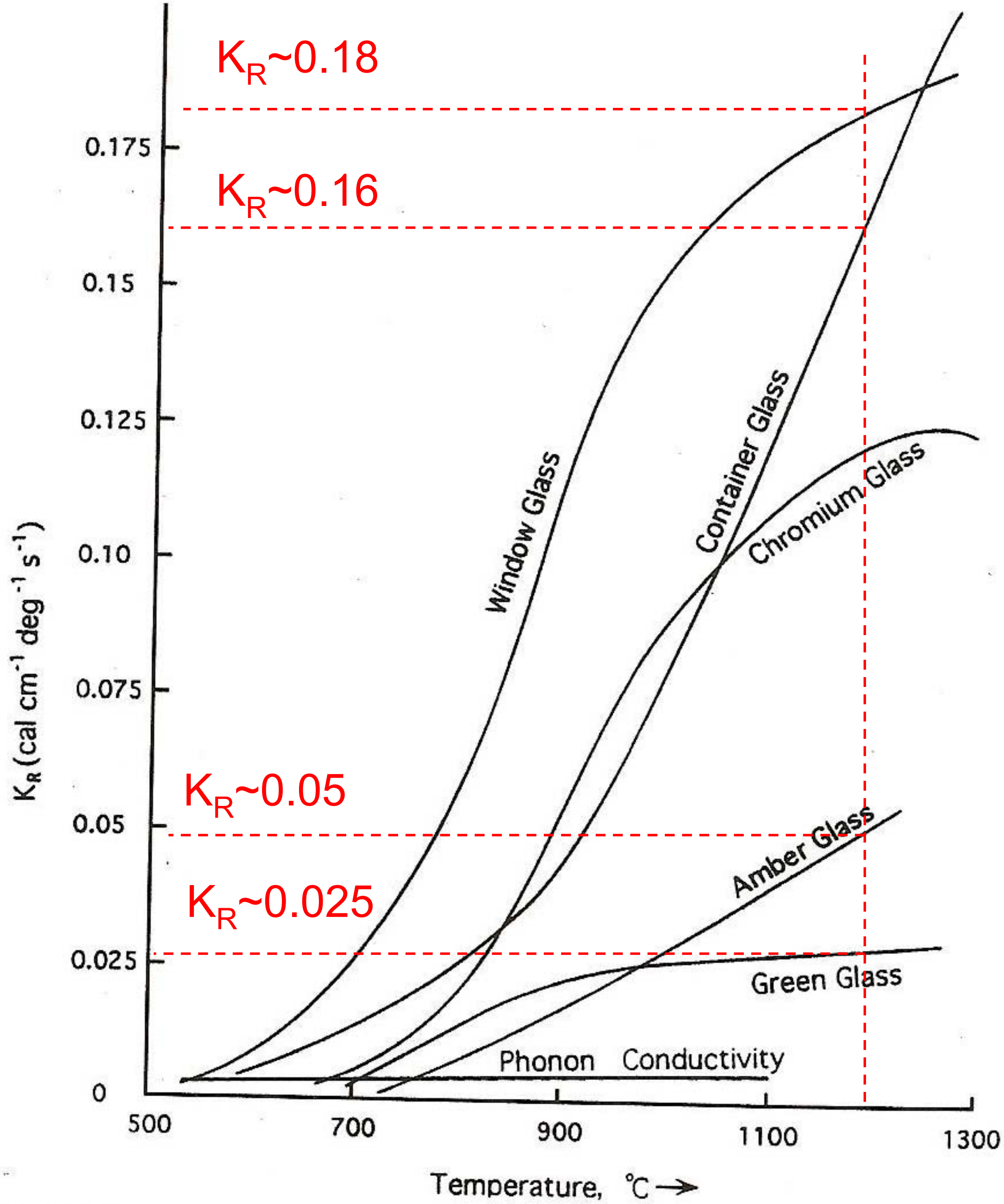
from Beerkens (1997)

Radiative conductivity (K_R): energy transfer by photons

$$K_R = 16n^2\sigma T^3 / 3\alpha$$

n=refractive index
σ=Stefan's constant
T=temperature
α=absorption coef.

Note: $K_R >> K_C$ and K_R is reduced for melts with large absorbance (from transition metal ions: Fe^{2+}, Cr^{3+}, etc)



Implications for how glass melts can be heated

- Clear melts absorb $\lambda > 4.5 \mu m$ (surface heating)
  - Heat emitted from surface penetrates into melt
- Shorter wavelengths are absorbed deeper in the melt
- Heat transferred by radiation→ absorption→ transmission→ re-radiation→ re-absorption cascade
- Clear melts can be heated to depths of 4-5 feet
- Colored (absorbing) melts must be shallower, or must employ auxiliary heat sources to avoid cold spots

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Heat Transfer by Convection

- Heat transfer (watt/m^2) by melt flow currents

$$\Phi_{conv} = \rho \cdot c_p \cdot v \cdot \Delta T$$

ρ=density (kg/m^3)
c_p=specific heat (J/(kg·°C)
v=melt velocity (m/s)
ΔT=temperature gradient

- Becomes significant when v>>~5x10^{-6} m/s
  - in melters, v~10^{-3} m/s

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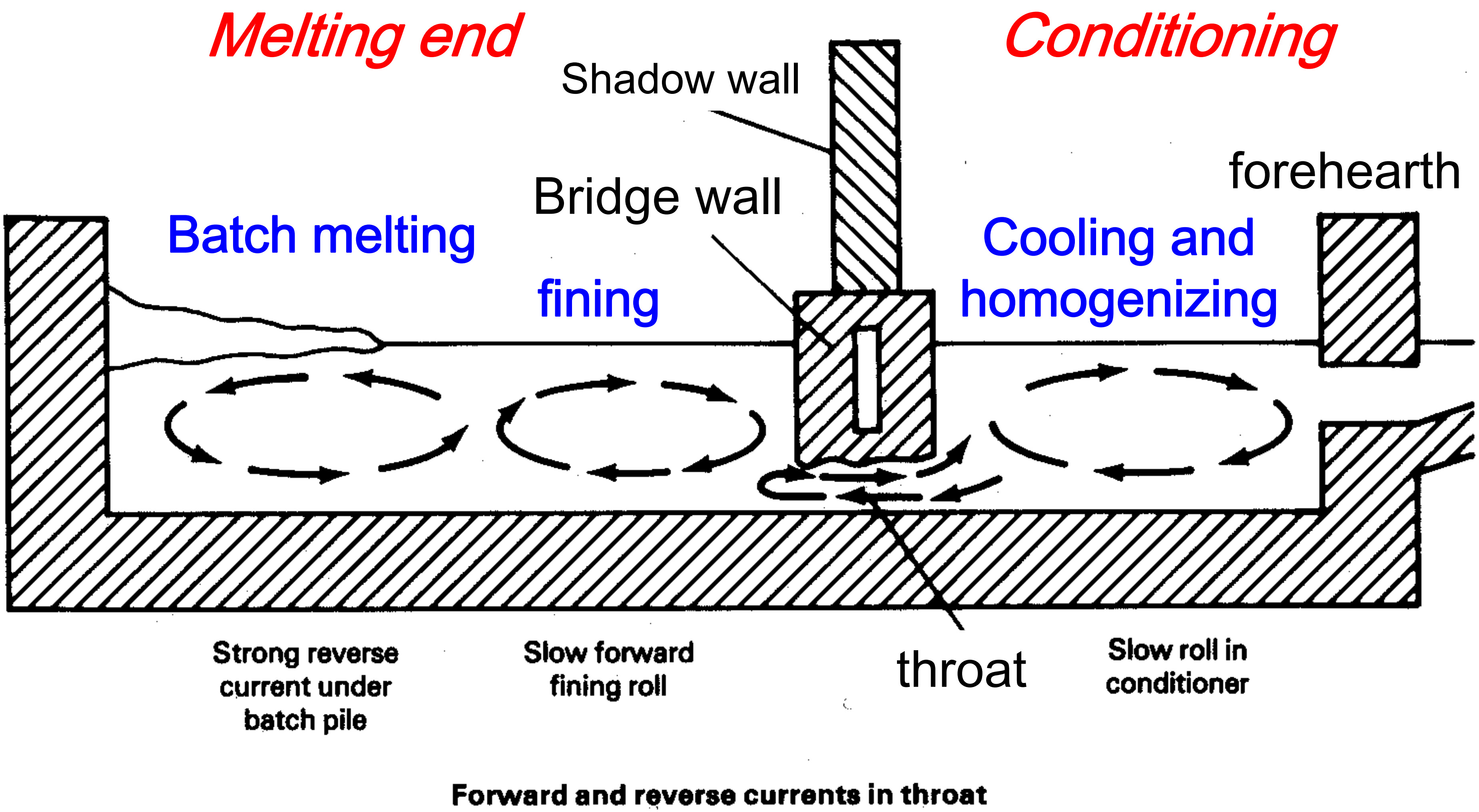
Major convective flows in tank furnace

(Wooley, *Engineered Materials Handbook*, **4** (1991), 386)



Melting end

Conditioning

Shadow wall

Bridge wall

forehearth

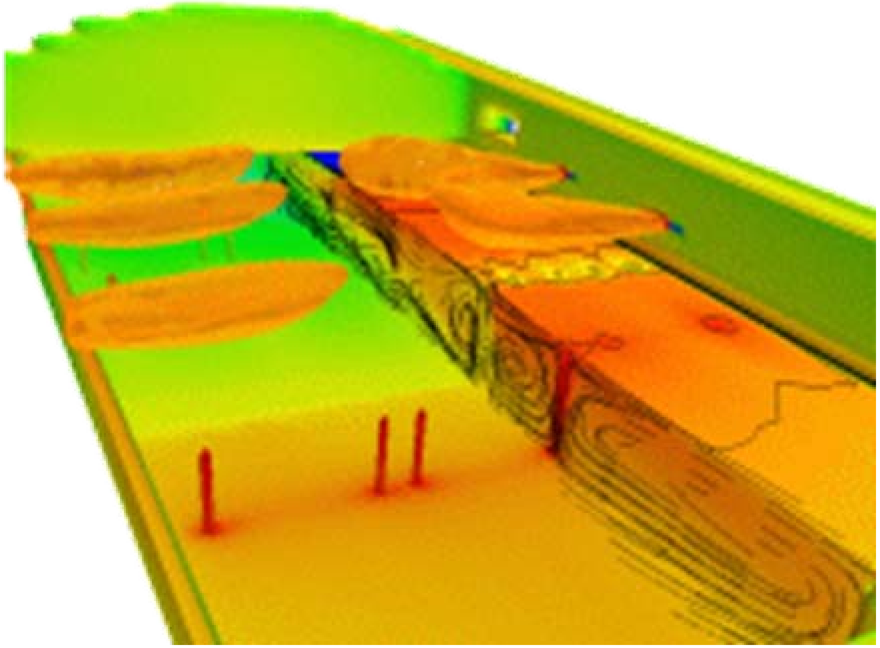
Batch melting

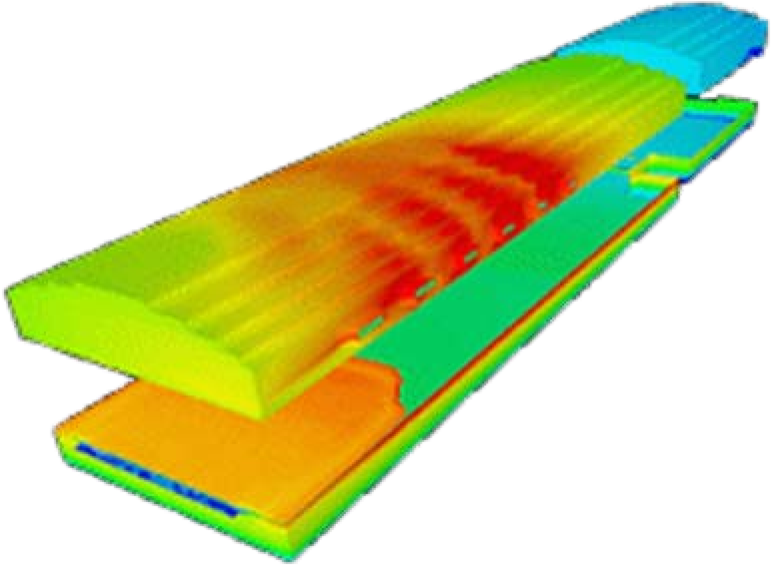
fining

Cooling and homogenizing

throat

Fig 3 Major convection flows in a fuel-fired tank furnace (longitudinal vertical section on tank centerline)





Thermal and transport modeling

- Temperature distributions
  - Combustion space
  - tank
- Flow patterns

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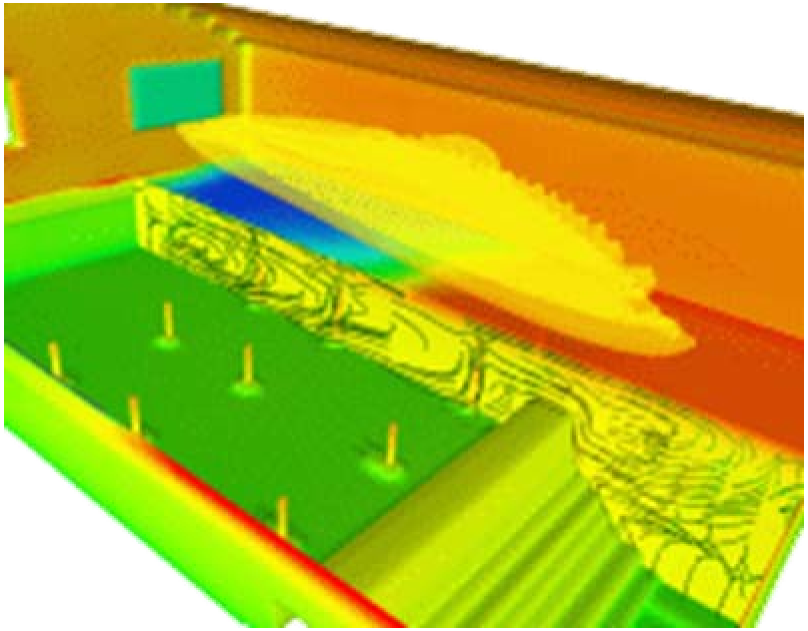

Summary

- Thermal properties are related to bond-strengths
  - Potential well determines CTE
  - Heat capacity / thermal conductivity (glass) depend on phonon energies
- Melt properties (surface tension, thermal conductivity and viscosity) depend on composition and define processing conditions