Optical and Photonic Glasses

Lecture 11:

Thermal Expansion of Glasses

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Thermal expansion of glass

Physical origin of thermal expansion: increase in *amplitude* of the thermal vibrations of the atoms/ions, as a result of their anharmonicity:

(a) anharmonic oscillator:

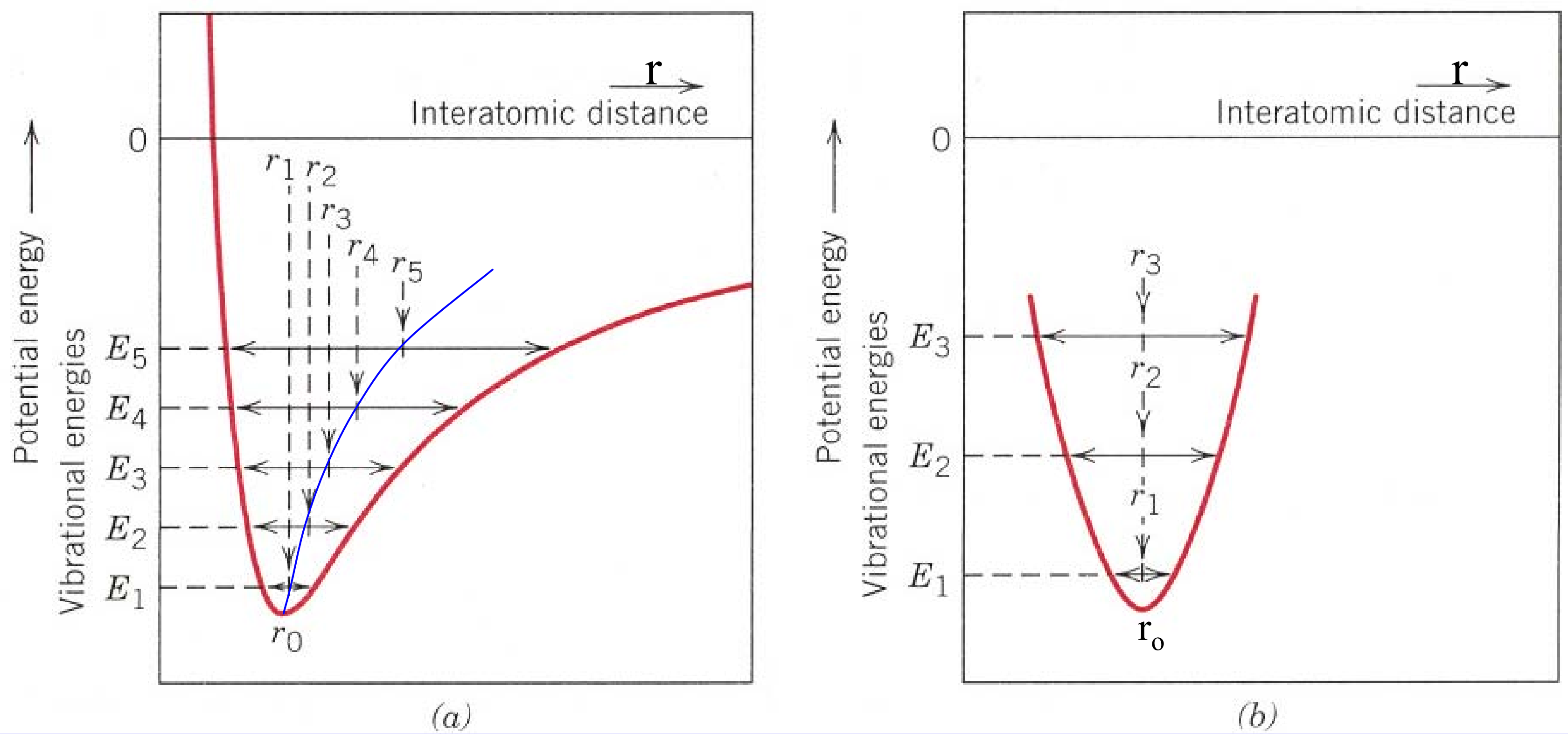
$V = ½ k (r-r_o)^2 + ...$

$E_v = (v + ½) h\nu + ...$

(b) *harmonic* oscillator:

$V = ½ k(r-r_o)^2$ (Hooke's law)

$E_v = (v + ½) h\nu$



(Adapted from: *Materials Science and Engineering*, W.D. Callister, John Wiley, 1994)

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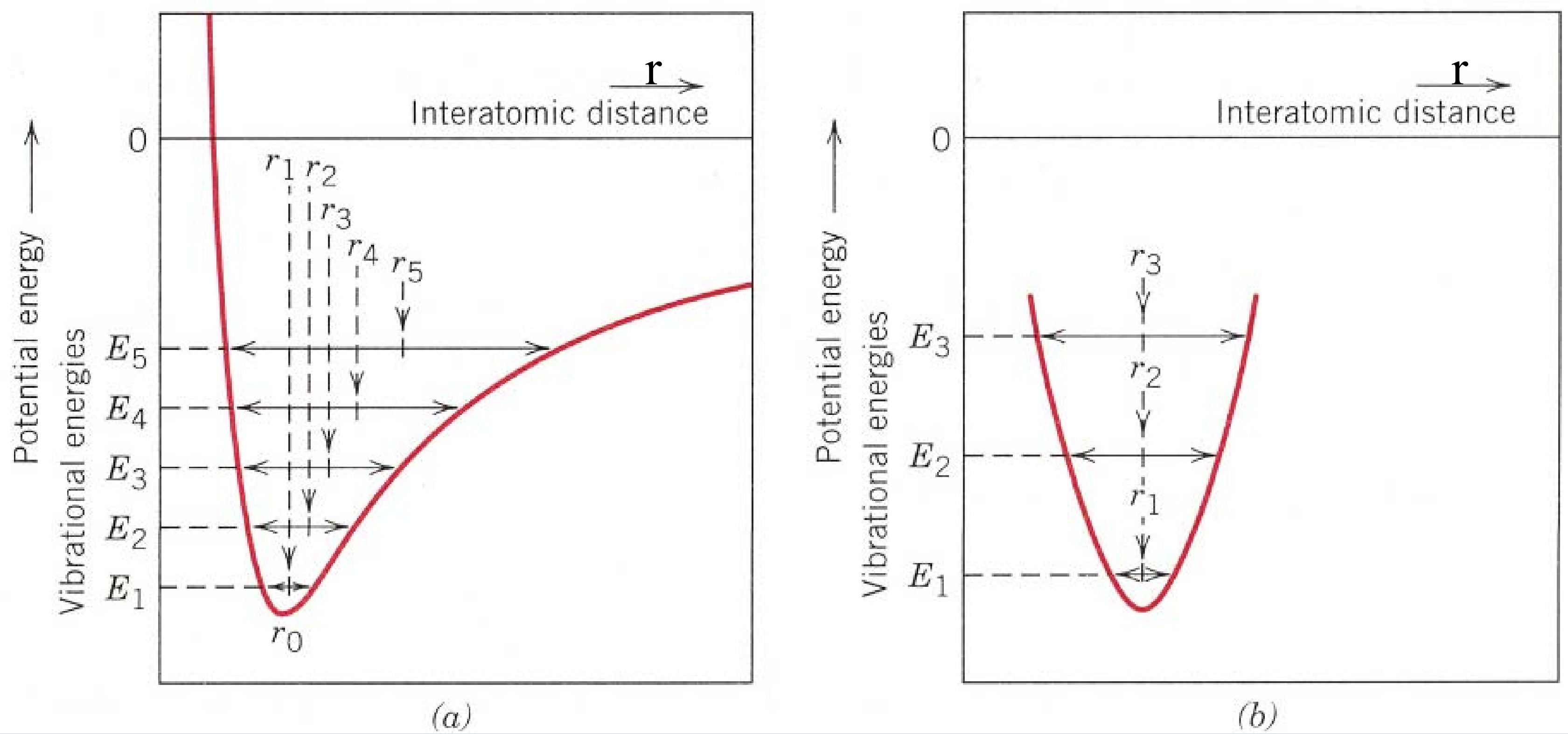

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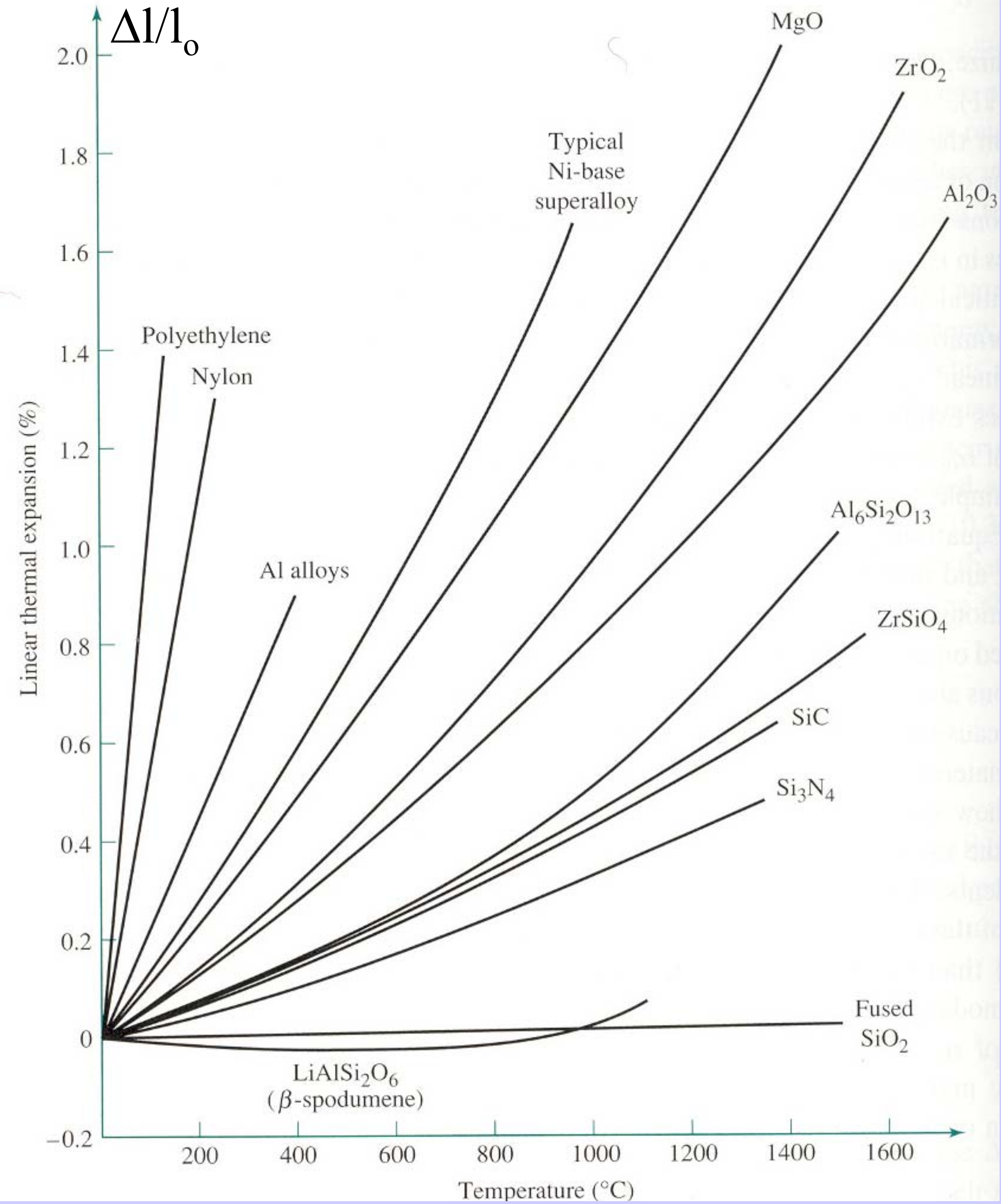
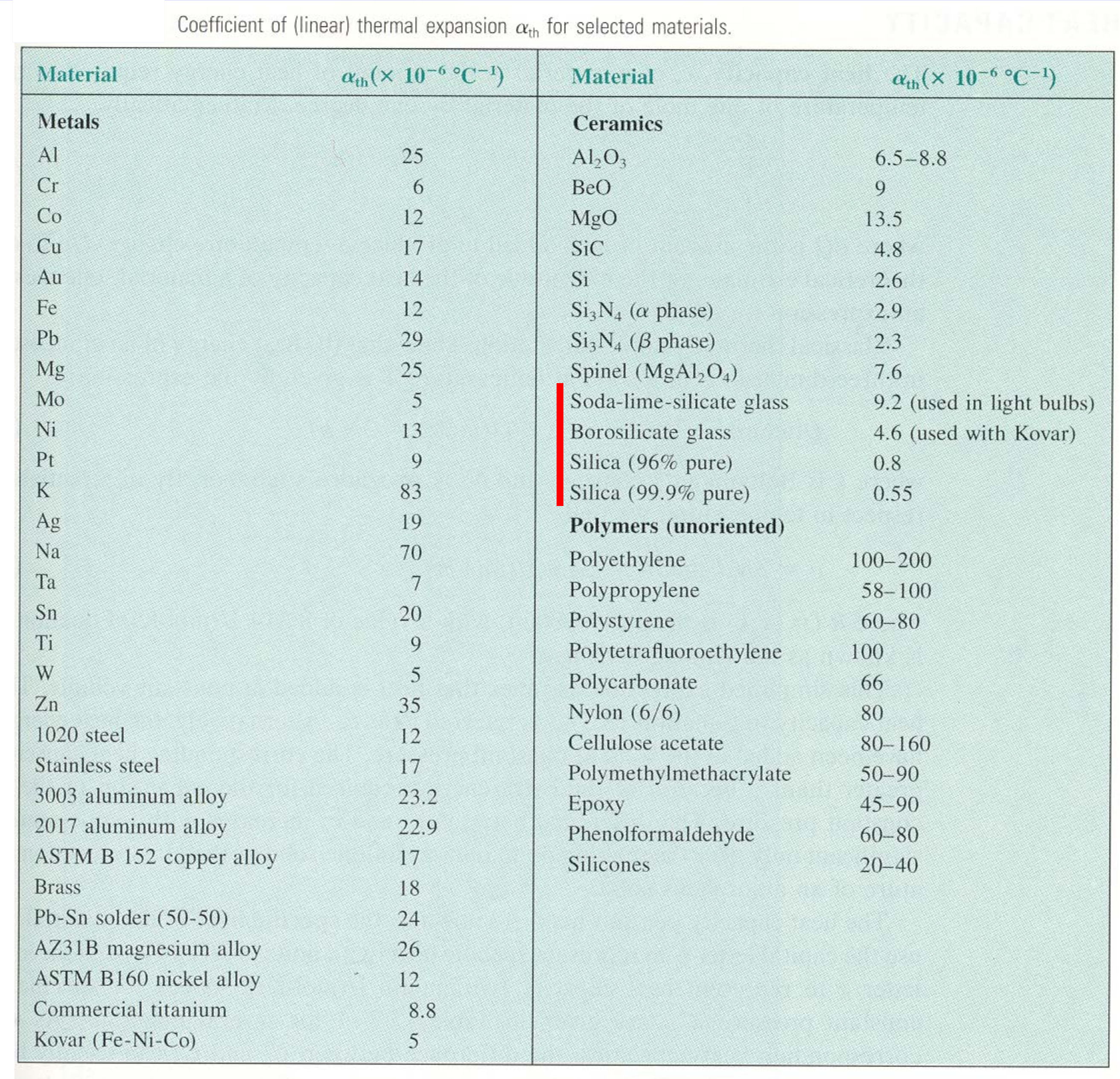


(Adapted from: *The science and design of engineering materials*, J.P. Schaffer et al., McGraw-Hill, 1999)



Coefficient of (linear) thermal expansion α_{th} for selected materials.

Material	α_{th} ($\times 10^{-6}$ °C^{-1})
Metals	
Al	25
Cr	6
Co	12
Cu	17
Au	14
Fe	12
Pb	29
Mg	25
Mo	5
Ni	13
Pt	9
K	83
Ag	19
Na	70
Ta	7
Sn	20
Ti	9
W	5
Zn	35
1020 steel	12
Stainless steel	17
3003 aluminum alloy	23.2
2017 aluminum alloy	22.9
ASTM B 152 copper alloy	17
Brass	18
Pb-Sn solder (50-50)	24
AZ31B magnesium alloy	26
ASTM B160 nickel alloy	12
Commercial titanium	8.8
Kovar (Fe-Ni-Co)	5

Material	α_{th} ($\times 10^{-6}$ °C^{-1})
Ceramics	
Al_2O_3	6.5–8.8
BeO	9
MgO	13.5
SiC	4.8
Si	2.6
Si_3N_4 (α phase)	2.9
Si_3N_4 (β phase)	2.3
Spinel ($MgAl_2O_4$)	7.6
Soda-lime-silicate glass	9.2 (used in light bulbs)
Borosilicate glass	4.6 (used with Kovar)
Silica (96% pure)	0.8
Silica (99.9% pure)	0.55
Polymers (unoriented)	
Polyethylene	100–200
Polypropylene	58–100
Polystyrene	60–80
Polytetrafluoroethylene	100
Polycarbonate	66
Nylon (6/6)	80
Cellulose acetate	80–160
Polymethylmethacrylate	50–90
Epoxy	45–90
Phenolformaldehyde	60–80
Silicones	20–40

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For a given temperature, T:

linear thermal expansion coefficient of a sample of length **l**:

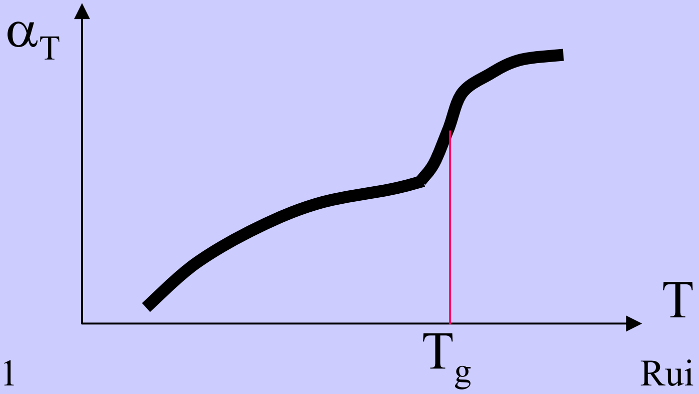
$$\alpha_T = (1/\mathbf{l})\, d\mathbf{l}/dT \qquad \text{(in units of } K^{-1}\text{)}$$

$$\alpha_T = 1/3\ \alpha_T^{vol} = 1/3\ (1/V)\ (\partial V/\partial T)_P$$

Over a small temperature range, the average value:

$$\alpha_T = (1/\mathbf{l}_{av})\ \Delta\mathbf{l}/\Delta T \sim (1/\mathbf{l}_o)\ \Delta\mathbf{l}/\Delta T = (1/\mathbf{l}_o)\ (\mathbf{l}-\mathbf{l}_o)/(T-T_o)$$

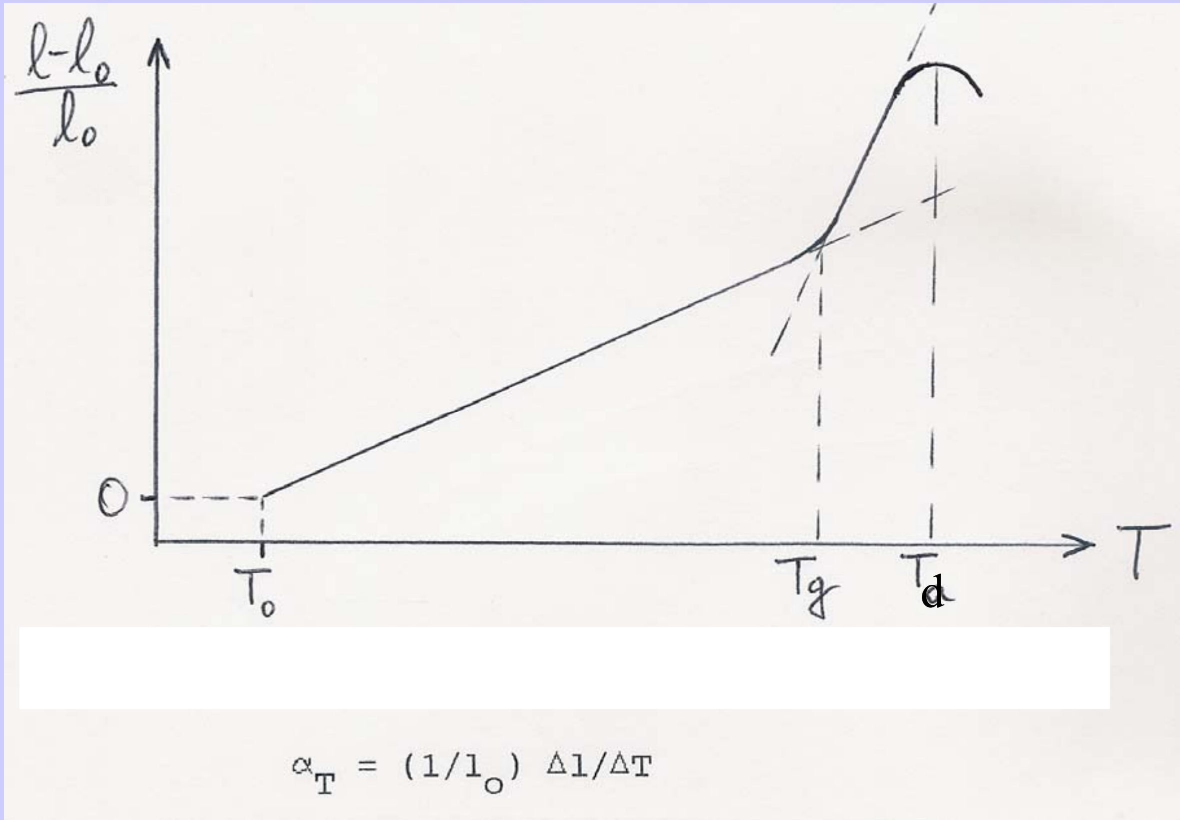
For a glass, the changes of α_T with T are similar to those of c_p:



Typical thermal expansion curve for a glass, with the relative expansion, $\Delta \mathbf{l}/\mathbf{l}_o$, plotted as a function of temperature. The *thermal expansion* coefficient is the slope of the curve. The slope increases steeply above T_g, hence this is a *good method to determine* the glass T_g. The *dilatometric softening temperature*, T_d, corresponds to $\eta \sim 10^9$-10^{10} Pa.s, a viscosity much higher than that of the Littleton softening point ($10^{6.65}$ Pa.s).

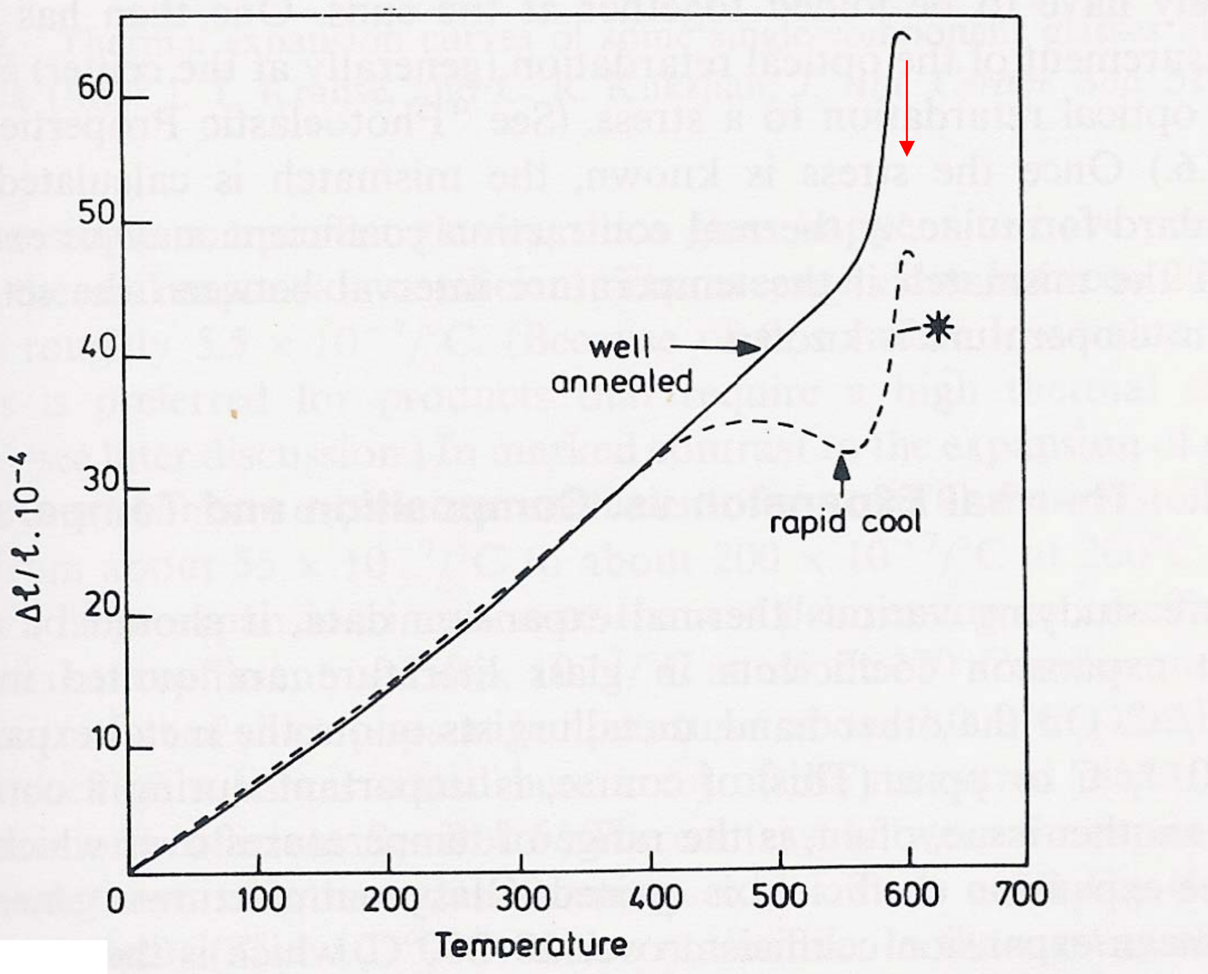
Usually, for modified SiO_2-R_2O silicate glasses of varying R_2O content, one has:

$$\alpha_T T_g \sim \text{constant} \qquad \text{or} \qquad \alpha_T T_g^2 \sim \text{constant}$$



$\alpha_T = (1/l_o)\, \Delta l/\Delta T$

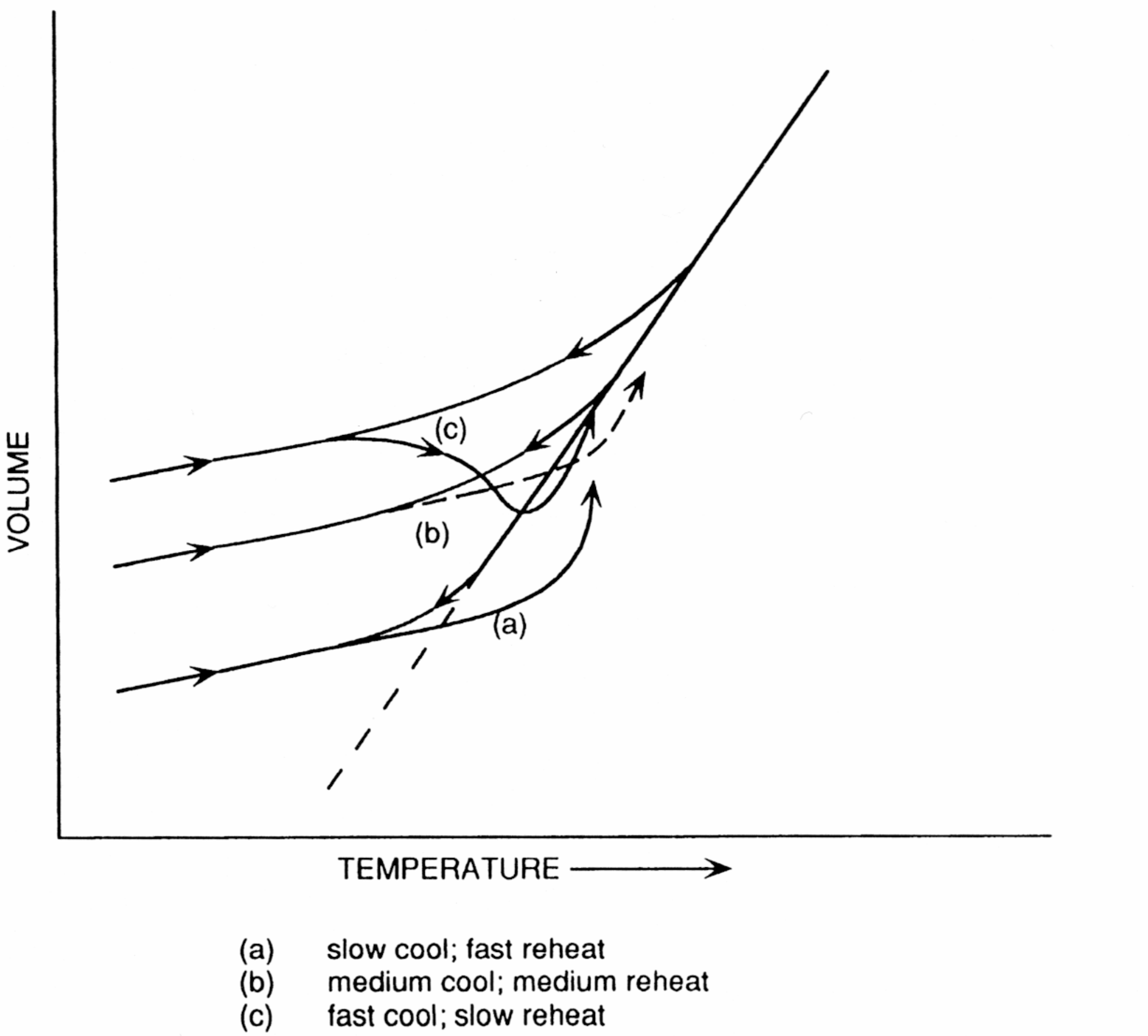
The curvature downwards is an artifact due to an apparent contraction caused by a pushrod penetration into the specimen, due to its softening. The rapidly cooled glass is less dense than the well annealed one and it will shrink, up to a certain point, when slowly reheated, as a result of structural relaxation.



Effect of the initial cooling rate on the expansion of a glass.

(Adapted from: *Fundamentals of inorganic glasses*, A.K. Varshneya, Academic Press, 1994)

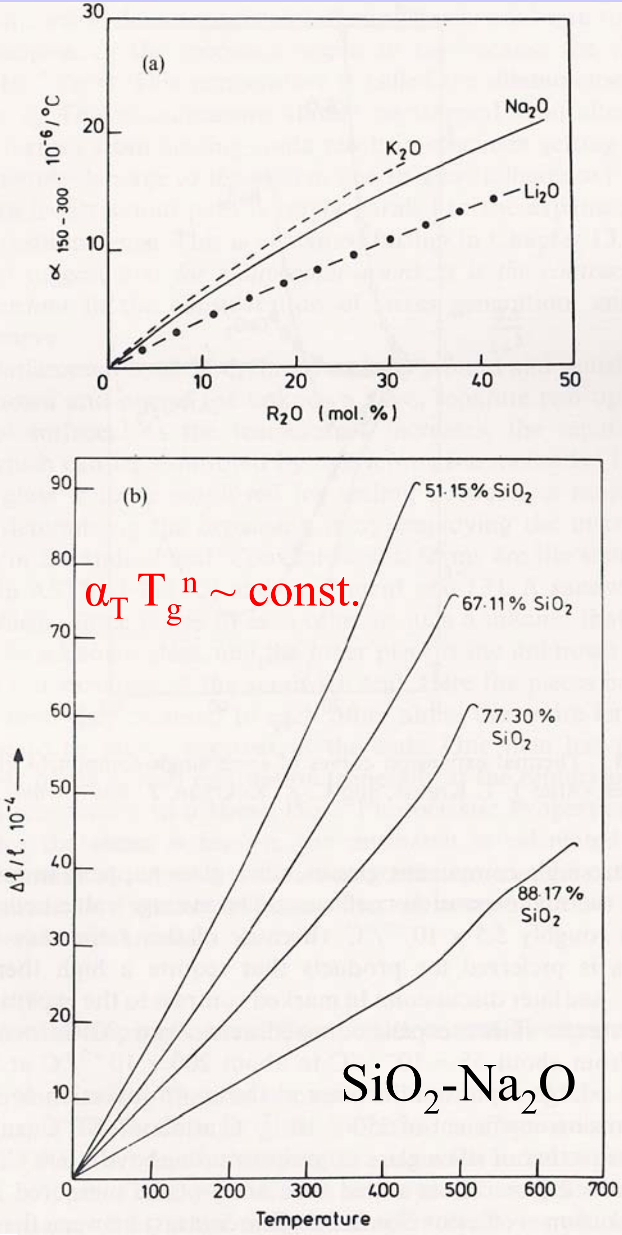
Volume structural relaxation



Volume changes in glass upon varying cooling and reheating rates.

(Adapted from: *Fundamentals of inorganic glasses*, A.K. Varshneya, Academic Press, 1994)

Thermal expansion coefficients and thermal expansion curves for alkali silicate glasses.



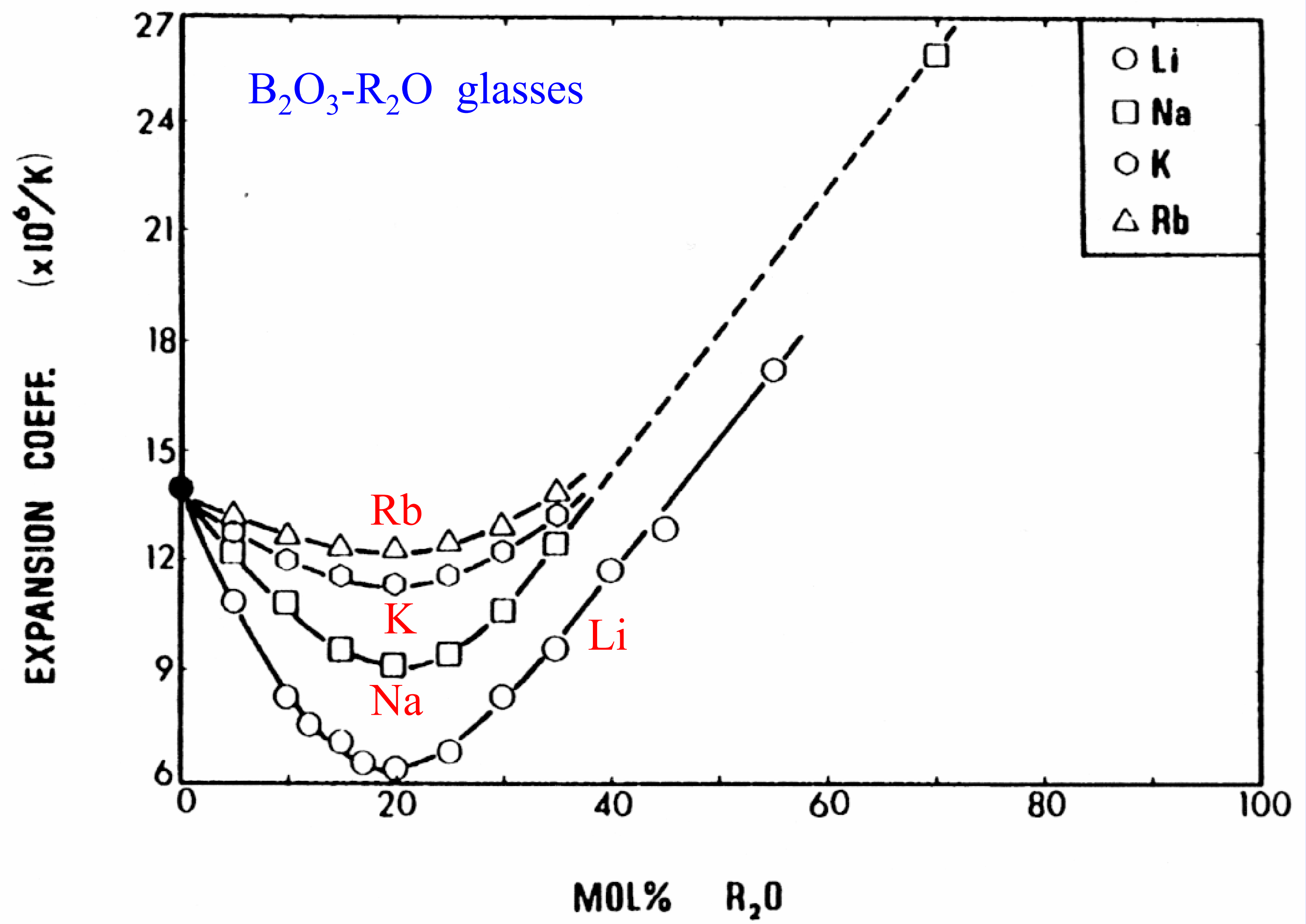
$\alpha_T T_g^n \sim$ const.

SiO_2-Na_2O

(a) Thermal expansion coefficients of R_2O–SiO_2 (R = Li, Na, K) glasses as a function of composition. (b) Thermal expansion curve for $x$$Na_2O$·(100 × x)SiO_2 glasses.

(Adapted from: *Fundamentals of inorganic glasses*, A.K. Varshneya, Academic Press, 1994)

Borate anomaly



Thermal expansion coefficients of $R_2O \cdot B_2O_3$ glasses as a function of composition. (After J. E. Shelby, *J. Am. Ceram. Soc.*, **66**(3), 225–227 (1983).)

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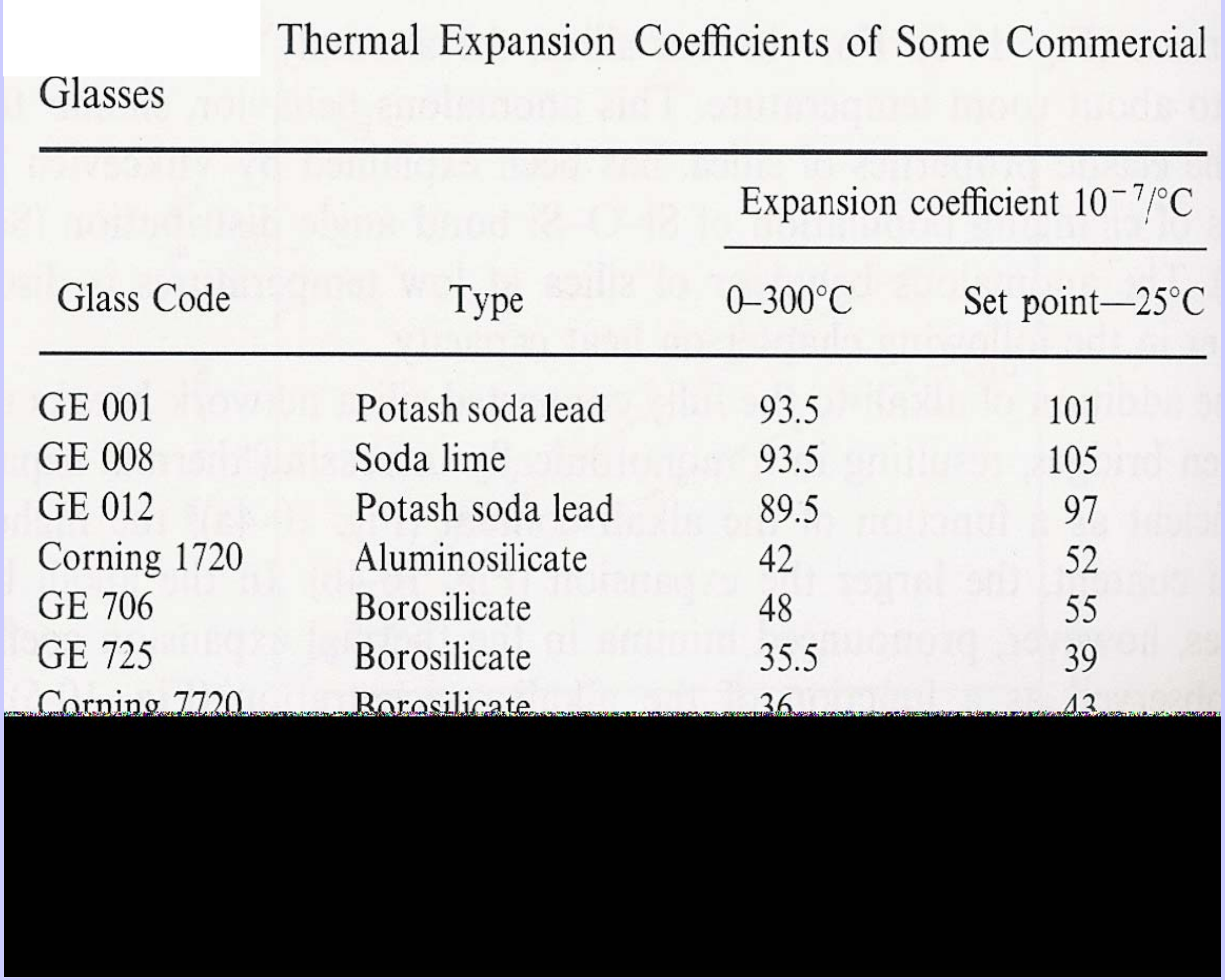

Thermal Expansion Coefficients of Some Commercial Glasses

		Expansion coefficient 10^{-7}/°C	
Glass Code	Type	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

[redacted]

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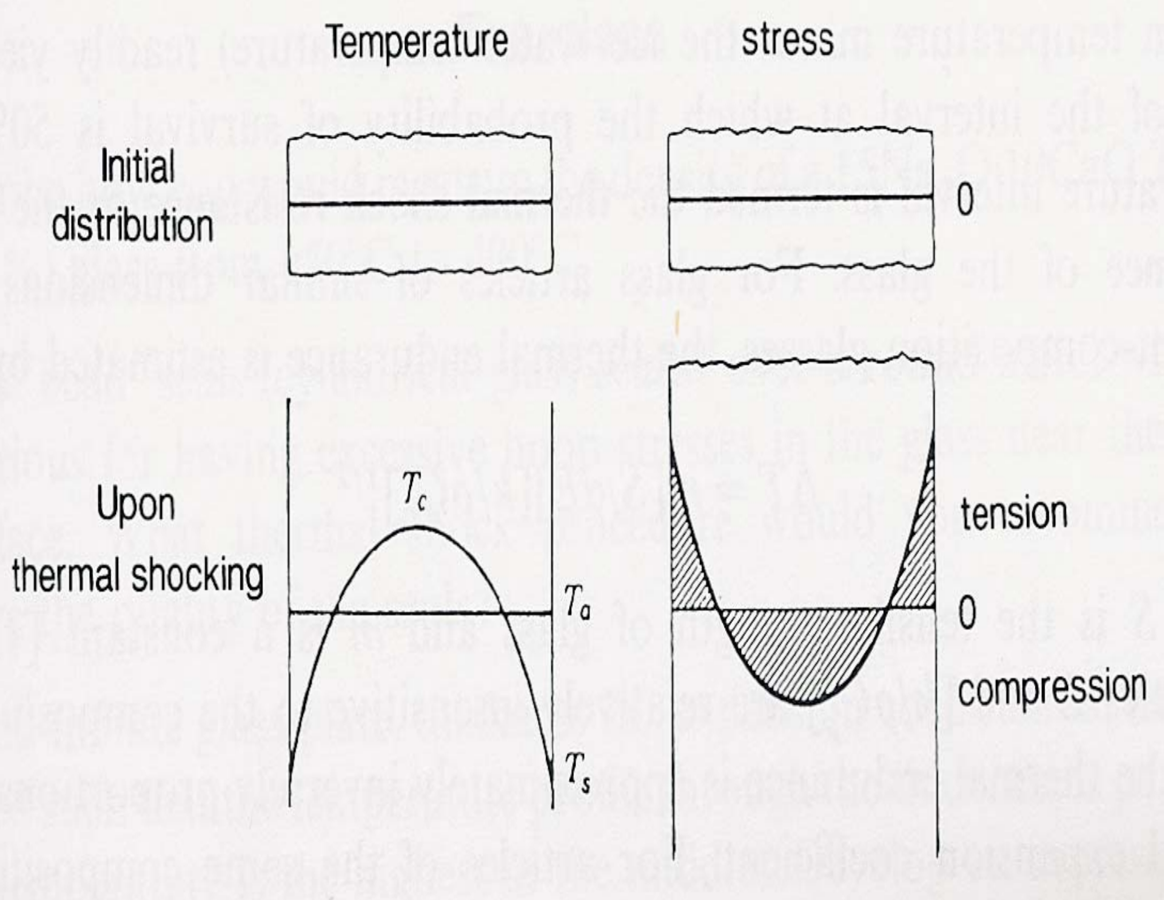
Sudden cooling of a glass surface below the average specimen temperature, T_a, causes the development of tensile stresses which can lead to glass fracture by *thermal shock*. The glass interior, where the temperature is above T_a and is maximum at the center, will be under compression. The thermal shock resistance is strongly dependent on the value of α_T and v-SiO_2 ($\alpha_T \sim 5\text{x}10^{-7}$ K^{-1}) has an exceptional resistance to thermal shock.



Stress production in glass due to thermal shock.

(Adapted from: *Fundamentals of inorganic glasses*, A.K. Varshneya, Academic Press, 1994)

Annealing and tempering

While the annealing of glasses at $T \leq T_g$ is performed to promote the release of residual thermal stresses created during casting (generally into a mold at a temperature lower than the melt), the mechanical resistance of the final glass may be increased by means of thermal or chemical tempering treatments.

The most common thermal tempering (performed, e.g., on different types of glass windows) starts with a sudden cooling of the surface of a glass part (initially near its Littleton softening point), by blowing cold air over it, through a nozzle. The surface quickly solidifies (under a moderate tensile stress), while the internal layers are still hot and viscous, but these subsequently contract upon cooling, solidifying under tension, which is then compensated by a residual *surface compression*.

The surface compression is the key point, since catastrophic propagation of glass surface flaws will only occur under a tensile stress after the surface compression has been offset by the applied tensile stress, corresponding to a *strengthening* of the *glass*. (Remember that, according to Griffith's theory, $\sigma_c = 8\ \sigma_t$).

Thermal tempering is not possible for very thin glass sheets, for glasses with very small α_T (e.g. high-silica glasses), or for complex shapes such as bottles, which are all cases where *chemical tempering* may be utilized.