Property trends (including density, refractive index, etc.) were used to develop structure/composition models before development of modern spectroscopic probes.   Borate anomaly from CTE study, 1934
        B[4] sites first detected in 1938 (X-ray diffraction).

Terminology:

1. *Density*   mass per volume ($\rho = m/V$)
   - *true density*- no bubbles, inclusions, etc.
   - *apparent density*- with defects (bubbles can reduce apparent density, crystalline inclusions can increase apparent density).

2. *Molar Volume*   volume occupied by one mole of material:

$$V_m = \frac{molar\ wt.}{density} = \frac{M.W.}{\rho} = \frac{g\,/\,mole}{g\,/\,cm^3} = \frac{cm^3}{mole}$$

Ex. $25Na_2O\ 75SiO_2$ glass: M.W. = $0.25 \cdot MW(Na_2O) + 0.75 \cdot MW(SiO_2)$
                                = 0.25(61.98 g/mole)+0.75(60.09 g/mole)
                                = 60.56 g/mole

        Density = 2.434 g/cm^3

        V_m = (60.56 g/mole)/(2.434 g/cm^3) = 24.88 cm^3/mol

Molar volume is more sensitive to structural differences between glasses than is density because it normalizes for atomic weights of different glass constituents.

Measuring Density

a.   *Archimedes' Method* is most convenient
   - Determine volume of displaced liquid
   - Sample weighed in air (W_{air}) and weighed when suspended in liquid (W_{liq}) of known density:
     - $\Delta W = (W_{air} - W_{liq}) = W$(displaced liquid)
     - sample volume = displaced liquid volume = $\Delta W / \rho_{liq}$
     - $\rho_{sample} = (W_{air} \cdot \rho_{liq}) / \Delta W$
   - generally accurate to ± 0.001 g/cm^3

b.   *Density Gradient Column*

- Low ρ liquid (e.g., isopropyl salicylate, 1.1 g/cm^2) poured onto a high ρ liquid (e.g. methylene iodide, 3.32 g/cm^3); liquids interdiffuse to establish gradient. (Gravity prevents uniform mixing).
- Glass samples sink to respective density levels
- Quick, accurate (± 0.0002 g/cm^3) test used in manufacturing environments
- ppm accuracies if similar liquids are used

1-1.5 m
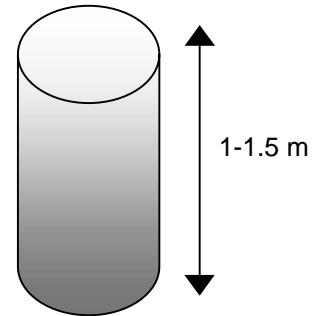
c.   *Sink-Float*
- Unknown sample dropped into tube containing slightly denser liquid
- Tube is heated until glass sample sinks
- From the known $\rho(T)$ relationship of liquid, you get the density of the glass
- Used to determine density differences (20 ppm) between similar samples (from ΔT_{sink}): e.g., Shelby's radiation effects studies

Compositional Effects

Densities of common glass forming oxides are less than the corresponding crystalline forms-glasses have more open network structures.

v-SiO$_2$	2.20 g/cm^3
α-quartz	2.65 g/cm^3 (Room T. form)
β-cristobalite	2.27 g/cm^3 (Hi.T. polymorph)
coesite	≈ 3.0 g/cm^3 (Hi pressure form)

'Free Volume' is the amount of open space in a glass structure (right). If the densest crystal represents 'ideal packing' for a composition, then the 'free volume' will be the difference in molar volumes between the glass and crystal:

$$V_f = V_g - V_x$$

The fraction of the total glass volume that is 'free' then is

$$(V_f/V_g) = 1 - (V_x/V_g) \qquad \text{Shelby, eq. 7.6}$$
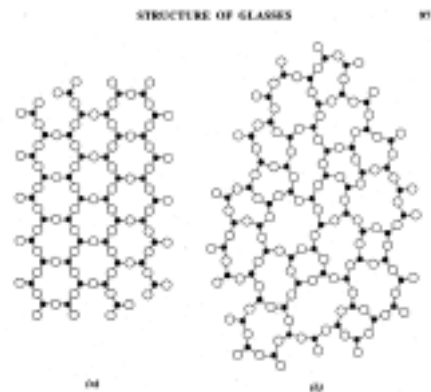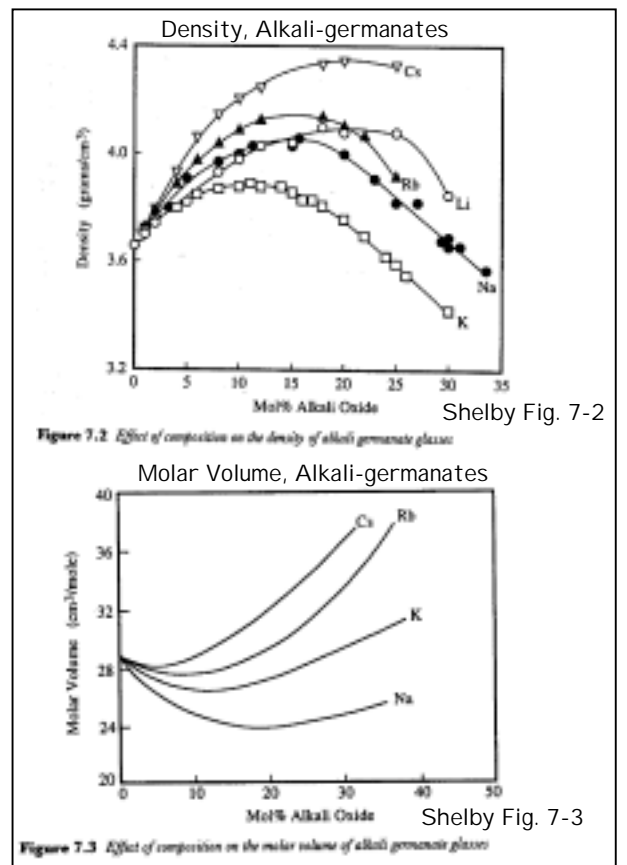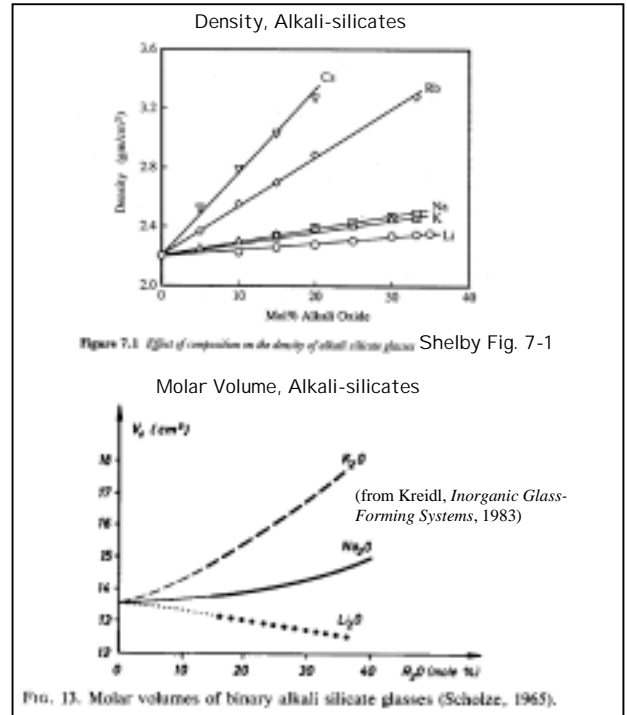
Using coesite density: the free volume in v-SiO$_2$ is 27%.

Adding alkali oxides typically increase density; alkali ions 'fill' the free volume.

- Shelby describes a 'sponge'- fill in the empty spaces without expanding the volume; so density increases.
  - Density increasing with alkali additions in the silicate glasses (top right) and that density increases in the order Li<Na<K<Rb<Cs
  - Molar volume trends (right bottom) suggest a little more complicated relationship: small ions (Li) have low coordination numbers, and so the structure collapses around them, leading to a MV decrease; whereas structure expands to accommodate the larger coordination numbers of the larger ions (Na, K, etc.)

- In the alkali germanate glasses , initial additions of modifiers increase density, then density goes through maxima because of the Ge[4]→Ge[6] transition.
- The 'just filling interstices' model breaks down when one considers that the K-germanates are less dense than the Li-germanates, despite the greater mass of the K-ion.
- The molar volume trends are a little more straightforward than the densities. The greater MV of the K-germanates (to accommodate the larger CN of K^+) offsets the larger atomic weight

Remember: alkalis have specific coordination environments that depend on their size. The high mobility of alkali ions near T_g ensures that alkali bonding is satisfied when the glass is cooled.

Density, Alkali-silicates

Figure 7.1 *Effect of composition on the density of alkali silicate glasses* Shelby Fig. 7-1

Molar Volume, Alkali-silicates

(from Kreidl, *Inorganic Glass-Forming Systems*, 1983)

Fig. 13. Molar volumes of binary alkali silicate glasses (Scholze, 1965).

Density, Alkali-germanates

Figure 7.2 *Effect of composition on the density of alkali germanate glasses*   Shelby Fig. 7-2

Molar Volume, Alkali-germanates

Figure 7.3 *Effect of composition on the molar volume of alkali germanate glasses*   Shelby Fig. 7-3

High Density Glasses: contain PbO, Bi_2O_3, Ga_2O_3, etc. $\rightarrow$8 g/cm^3.
- • -radiation windows, optical applications

Glasses will densify under radiation, pressure, etc.
- • structural compaction; stress generation
- • up to 3%

Fictive temperature effects
- • Room temperature density is sensitive to thermal history (discussed previously).
- • Silica is unusual. Room temperature density of glasses heated at various temperatures above T_g (right, Shelby 7-6) goes through a maximum. The 'melt density' goes through a maximum on heating; very unusual.
  - • Behavior eliminated with small additions of second oxide.
  - • Water exhibits similar density maximum at 4°C.
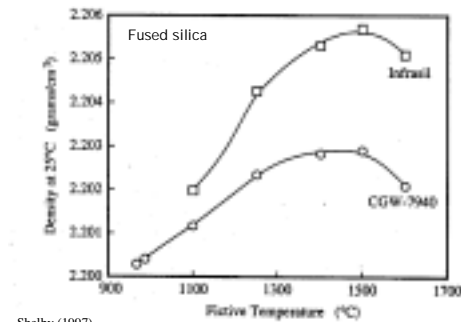
Shelby (1997)
Figure 7.6 *Effect of fictive temperature on the density of vitreous silica*

3. Thermal Expansion Coefficient

- • Rate of change in volume (and therefore, density) with temperature
- • True (or instantaneous) thermal expansion coefficient:

$$\alpha_v = \frac{1}{V_0}\left(\frac{\partial V}{\partial T}\right)_P$$

Volume vs **Temp**, slope α_v
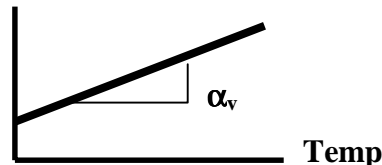
- • *more common is the average (or mean)* TEC (or CTE), defined by a change in volume (ΔV) over a specified temperature range:

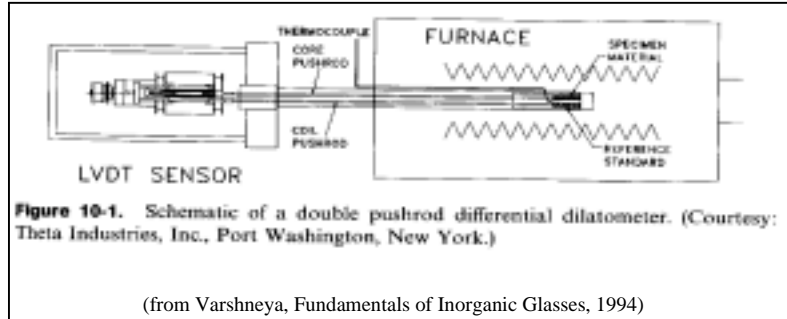$$\overline{\alpha}_v = \frac{1}{V_0}\left(\frac{\Delta V}{\Delta T}\right)$$

- • volume changes are difficult to measure, linear changes are much more simple and a typical TEC is based on a length-change measurement:

$$\alpha_l = \frac{1}{l_0}\left(\frac{\Delta l}{\Delta T}\right)$$

- • Since glasses are isotropic (and have relatively small TECs): $\alpha_v = 3\alpha_l$
  - • units are in (degrees)$^{-1}$

- Typical TEC ranges for glasses are $5\times10^{-7}/°C$ to $150\times10^{-7}/°C$ (or 0.5 to 15 ppm). Commercial silicates are in the range $70\text{-}100\times10^{-7}/°C$.

Dilatometry is the preferred TEC measurement technique.

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

(from Varshneya, Fundamentals of Inorganic Glasses, 1994)

Single push rod dilatometer: measure absolute expansion/contraction.
Dual push rod dilatometer: measure difference with known reference.

- Generally accurate to 0.5%

Shelby's Fig. 7-8 shows examples of TEC curves

T_g defined as the temperature at which the expansion behavior changes from 'solid-like' to 'liquid-like'. Determined from the crossover of the extended lines.

T_d is the dilatometric softening point, the temperature at which the spring-loaded pushrod deforms the sample because the glass viscosity is too low to withstand the applied load.
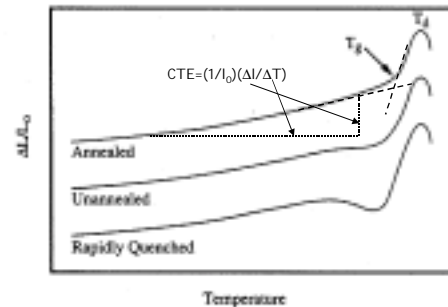
Figure 7.8 *Thermal expansion curves for annealed and quenched glasses*

Relaxation of the high fictive temperature (unannealed) sample produces the dip in the CTE curve as the glass structure rearranges in the transformation range. (This is a good test for the degree of annealing in a sample).

More accurate TEC's (to 20 nm displacements) can measured by laser interferometry.

Concepts of Thermal Expansion

Condon-Morse potential: interaction energy between a cation and anion is a balance between the Coulombic attraction and the internuclear repulsion (the latter occurs because of overlapping electron orbitals if ions are brought too closely together.)
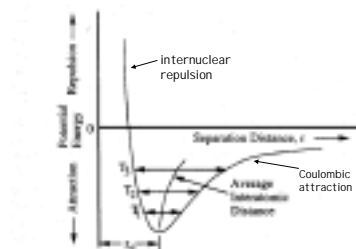

Shelby (1997)

Figure 7.7 *Condon-Morse curve illustrating the cause of the thermal expansion of bonds*

- Ideal separation distance (r_0) at 0 K.
- The well determines how the atoms vibrate- can't come to close together because of the repulsion, too far apart or there will be no 'restoring' Coulombic attraction.
- Increase temperature, initiate thermal vibrations, progress 'further up the well'.
- Deep wells- high dissociation energies (high melting/boiling points).
- Because of the asymmetry of the potential well, the average separation distance, due to thermal vibrations, increases with temperature, representing an expansion in the lattice (TEC).
    - Deep wells are more symmetric, and so represent low TEC materials
    - Shallow wells become asymmetric at smaller ΔT:
        - Lower melting materials generally have greater TEC's

Shelby relates compositional changes that affect bond symmetry (i.e., formation of NBO's with alkali additions) to changes in the symmetry of a C-M well:
- Alkali additions to silicate glasses increase TEC
- Alkali additions to borate glasses decrease TEC

(from Varshneya, *Fundamentals of Inorganic Glasses*, 1994)

Changes in 'free volume' can also affect TEC. High free volume allows bonds to rotate and flex instead of stretch with increasing temperature, yielding low (or negative) TEC's (i.e., f-SiO_2). Filling up the 'free volume' (adding alkalis) eliminates this mechanism, increasing TEC.
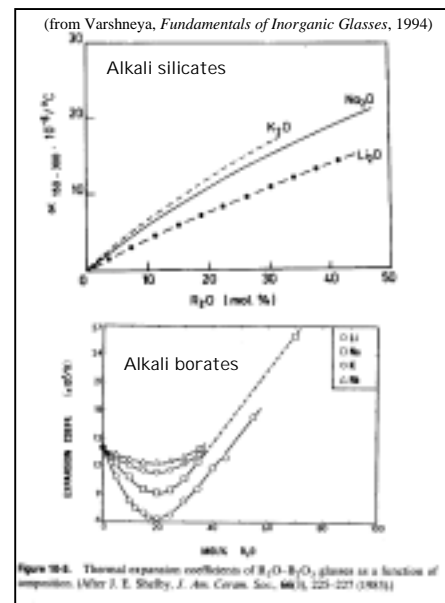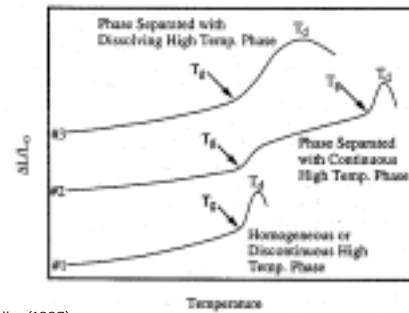
Oxide glass TEC's can be varied from 0 (SiO_2-TiO_2 'ULE' glasses for mirror blanks) to over 200×10^{-7}/°C for specialty phosphate sealing glasses.
- Wide range of glasses available for sealing applications, compatible with metals, ceramics with different TEC (matched, compression seals.)
- Note: The quoted TEC for a glass is over a specified temperature range. TEC will vary with ΔT- must be known when selecting an appropriate sealing glass.
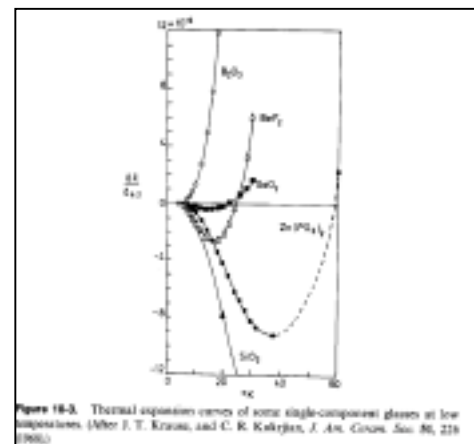
Phase Separation can be characterized by
TEC curves (Shelby Fig 7-11, right).

- Bottom curve- homogeneous glass (or
  phase separated where high temp. phase
  is discontinuous)
- Middle curve: phase separated, with a
  continuous high temp. phase.
- Top curve, broad softening region from
  glasses where rising sample temp. passes
  immiscibility or spinodal limits- changing
  morphologies.
- Practical Note: $(T_d-T_g)<50$ K, glass is
  probably phase separated

Crystallization will also alter TEC properties-

- Low-expansion glass-ceramics: cookware,
  mirror blanks, etc.
- High expansion glass-ceramics (right).
  - Cristobalite, a high expansion silica
    polymorph (note transition near 150°C);
    also note residual glass transition for
    700°C heat treatment, no residual T_g
    (top) for 800°C heat treatment.

Shelby (1997)
Figure 7.11 *Effect of phase separation on the thermal expansion curves of glasses*