Density and Thermal Expansion

1 INTRODUCTION

Trends in the density, thermal expansion coefficient, refractive index, and viscosity of glasses, as a function of bulk composition serve as the basis for many of the common structural models used today. These models were generated long before Raman, NMR, and other modern spectral techniques were developed. While details of these models have been refined using more sophisticated methods, the basic concepts of network structures, bridging and non-bridging oxygen formation, and changes in coordination number with changes in composition were originally proposed in an attempt to explain trends in property behavior. This approach to glass structure remains common even today, with many structural models proposed on the basis of property studies and later confirmed by the results of spectral studies.

2 TERMINOLOGY

The *density* of a material is defined as the mass of the substance per unit of volume:

$$\rho = \frac{M}{V} \tag{7.1}$$

where ρ is the density, M is the mass, and V is the volume of the sample. If the sample is free of bubbles, voids, or other defects, the calculated density is the *true density* of the material. If, however, the sample contains bubbles, which is occasionally the case for glasses, the calculated density will be less than that of the true density and is termed the *apparent density*. Inclusions with higher densities than the true density, which might, for example, be due to particles of unmelted batch

The *molar volume* is defined as the volume occupied by one mole of a material and is obtained by dividing the molecular weight of a material by its density:

$$V_m = \frac{MWt}{\rho} \tag{7.2}$$

where V_m is the molar volume, MWt is the molecular weight of the substance, and ρ is the true density of the material. Since the density of a material is sensitive to both the volume occupied by the atoms and to their mass (atomic weight), molar volume is often used to compare the behavior of glasses. In many cases, seemingly anomalous behavior in density is readily explained by consideration of the molar volume.

The method used to represent the formula of a glass can alter the calculated V_m by altering the value used for the molecular weight. The most commonly used definition of molecular weight is based on the oxide formulation method with mole fractional contributions from each component. The molecular weight of a $25Na_2O–75SiO_2$ glass is equal to the sum of 0.25 times the molecular weight of Na_2O plus 0.75 times the molecular weight of SiO_2. If we use molecular weights of 61.981 for Na_2O and 60.084 for silica, we obtain a molecular weight of 60.558 for this glass. Using a measured density of 2.434 g cm^{-3}, we find that the molar volume of this glass is 24.88 cm^3 per mole. While molar volume is

The *thermal expansion coefficient* of a material is a measure of the rate of change in volume, and therefore density, with temperature. The *true* (sometimes called *instantaneous*) *thermal expansion coefficient* is defined as the slope of the volume *versus* temperature curve, at a specified temperature and constant pressure (usually 1 atmosphere):

$$\alpha_V = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \tag{7.3}$$

where α_v is the true volume expansion coefficient, V is the volume of the sample, and $(\partial V/\partial T)_P$ is the slope of the curve. The *average*, or mean, *thermal expansion coefficient*, $\bar{\alpha}_v$, which is much more commonly reported, is defined by the change in volume, ΔV, over a specified temperature interval, ΔT:

$$\bar{\alpha}_V = \frac{1}{V}\left(\frac{\Delta V}{\Delta T}\right) \tag{7.4}$$

Although the thermal expansion coefficient is actually defined in terms of the volume of the substance, this value is somewhat difficult to measure. As a result, the expansion coefficient for glasses is usually only determined in one direction, *i.e.*, the measured value is the *linear thermal expansion coefficient*, α_l. The true and average linear thermal expansion coefficients are given by Eqs. 7.3 and 7.4, respectively, where V is replaced by L in each equation. Since glasses are usually isotropic materials with relatively small thermal expansion coefficients, $\alpha_v = 3\alpha_L$ can be used to approximate α_v with very little error in calculation.

Virtually all reported thermal expansion coefficients for glasses are actually average linear thermal expansion coefficients over some specified temperature range. The particular temperature range represented by this value is not always specified in the reported data. Data for commercial glasses are usually obtained for either the range from 0 to 300 °C, 20 to 300 °C, or 25 to 300 °C. Data for experimental studies may be reported for almost any temperature range, so caution must be used when comparing results from different studies. Since the true thermal expansion coefficient can be a strong function of temperature, knowledge of the temperature range used to define an average thermal expansion coefficient is vital for application of the data.

Since most linear thermal expansion coefficients lie between 1 and $50 \times 10^{-6}\ \mathrm{K}^{-1}$, metallurgists, ceramists, and other material scientists usually report values with units of ppm K^{-1}. Traditionally, however, glass technologists used $10^{-7}\ \mathrm{K}^{-1}$ as the basis for reporting thermal expansion coefficients. A glass technologist might, therefore, indicate that the linear thermal expansion coefficient for a certain glass is 86, while a ceramist might indicate the same coefficient as 8.6. Since older

3 MEASUREMENT TECHNIQUES

3.1 Density

The most direct method for determining density involves weighing a sample of known geometry, calculating its volume from its dimensions, and using Eq. 7.1 to calculate the density. If the available samples do not have simple geometries, we can use Archimedes' principle to determine the volume by liquid displacement. The sample is weighed both in air and suspended in a liquid of known density. The difference in weight equals the weight of the displaced liquid. Since we know the density of the liquid, ρ_L, we can calculate the displaced volume using Eq. 7.1. Dividing the weight of the sample in air, W, by the volume of liquid displaced then yields the density of the sample. The density is calculated from the expression:

$$\rho = \frac{W \rho_L}{(W - W_s)} \tag{7.5}$$

where W_s is the suspended weight of the sample. The choice of the

Densities of glasses are frequently measured by suspension in heavy liquids. A density gradient column is formed by introducing two liquids of different densities in continually varying proportions into a tall glass cylinder. A set of standards of known densities are then placed into the column. Since each standard will float at a depth where the liquid density equals that of the standard, a calibration graph of density versus depth can be plotted. A sample is placed in the liquid and allowed to come to rest at an equilibrium depth. The density is then read from the calibration plot. If the densities of the two liquids are very similar, these measurements are capable of detecting density differences of as little as 1 ppm among a set of nearly identical samples.

Sink-float methods are commonly used for quality control measurements for glasses. A sample is placed into a test tube containing an organic liquid which is slightly more dense than the sample. The tube is heated until the density of the liquid becomes less than that of the sample, whereupon the sample will begin to sink. If the test tube also contains a standard of known density, the difference in temperature at which the sample and standard sink can be used to calculate the difference in their densities, provided the temperature dependence of the density of the liquid is known. This method is capable of detecting differences in density of as little as 20 ppm.

3.2 Thermal Expansion Coefficients

Almost all reported thermal expansion coefficients for glasses have been obtained using some variation of a push-rod dilatometer. In its simplest form, a push-rod dilatometer consists of a cylinder of a material of known thermal expansion coefficient, which is fixed in place at one end and surrounded by a heating device. A sample is placed inside and against the end of this cylinder. A rod of the same material as the cylinder is placed against the sample. The other end of the rod is connected to some device capable of measuring very small changes in the position of the end of the rod. Heating the region containing the sample results in expansion of the surrounding cylinder, the rod, and the sample. If the sample has a different thermal expansion coefficient from that of the apparatus, the end of the rod will be displaced by an amount determined by the sample length and by the difference in thermal expansion coefficients between the sample and the apparatus material. Determination of the true thermal expansion coefficient of the sample requires correcting the displacement versus temperature data for the expansion of the apparatus.

Most dilatometers used in studies of glasses are constructed from vitreous silica. Since the average linear thermal expansion coefficient of vitreous silica is only about 0.55 ppm K^{-1} over typical temperature ranges covered in these measurements, the correction factor for the apparatus expansion is quite small. Furthermore, since virtually all glasses have glass transformation temperatures less than that of vitreous silica, the upper use temperature of ≈ 1000 °C imposed by the viscosity of this material is rarely of concern.

A more sensitive and accurate dilatometer can be constructed by use of two push-rods in an arrangement which measures the difference between the expansions of the sample and a reference standard. This

4 DENSITY AND MOLAR VOLUME

The density of a glass is a strong function of its composition. Density is also dependent to a lesser extent on the measurement temperature and the thermal history of the sample. Changes in morphology can have a small effect on density for phase separated glasses. Crystallization of a glass can significantly alter the density, if the density of the crystalline phase is very different from that of the residual glass.

4.1 Compositional Effects

Densities of the common glass forming oxides are less than those of the corresponding crystalline forms of these compounds. Vitreous silica, for example, has a density of ≈ 2.20 g cm^{-3}. This value can be compared with the densities of α-quartz (the room temperature crystalline form of silica) of 2.65 g cm^{-3}, β-cristobalite (the least dense crystalline form of silica) of 2.27 g cm^{-3}, and coesite (a very dense crystalline form of silica obtained at high pressures) of ≈ 3.0 g cm^{-3}. If we calculate the *free volume*, V_f, of the glass using the simple relationship:

$$V_f = 1 - \frac{V_x}{V_g} \tag{7.6}$$

where V_x is the molar volume of the crystalline form and V_g is the molar volume of the glass, we obtain a value of 0.27, or 27%, for vitreous silica, if we base our calculation on the dense crystal coesite. This large free volume implies that the glass has a very large fraction of interstitial space within the network for accommodation of other ions such as the monovalent alkali ions and the divalent alkaline earth ions.

does not swell as it absorbs the liquid). Indeed, we find that the addition of alkali ions to any of the common glass forming oxides results in an increase in density (Figures 7.1 and 7.2). Even Li_2O, which has only half the molecular weight of silica, increases the density of silicate, borate, or germanate glasses when substituted for the basic glass forming oxide.

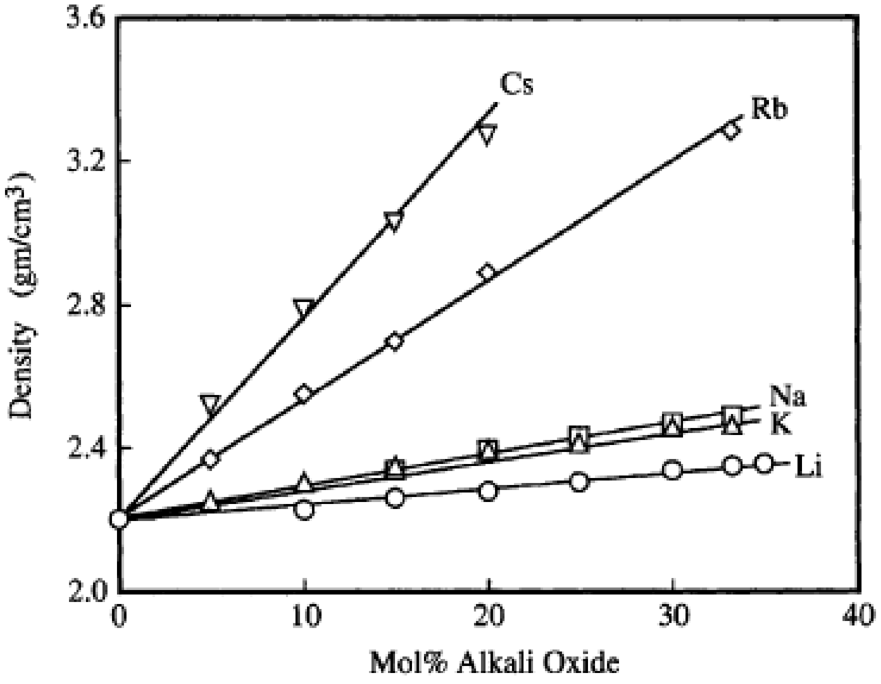

Figure 7.1 *Effect of composition on the density of alkali silicate glasses*

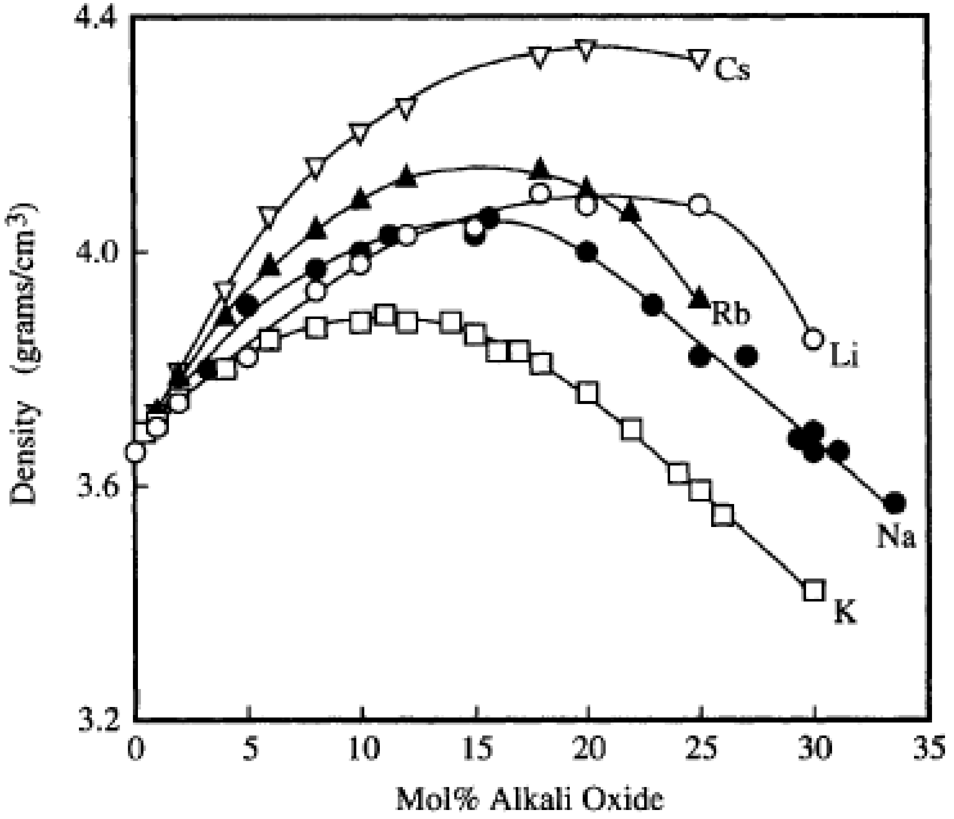

Figure 7.2 *Effect of composition on the density of alkali germanate glasses*

The most dense oxide glasses contain very high concentrations of PbO or Bi_2O_3, with maximum values in the range of 8.0 g cm^{-3} for glasses in the $PbO–Bi_2O_3–Ga_2O_3$ system. The rather low maximum

4.2 Thermal History Effects

While the densities of crystalline materials are not particularly sensitive to the thermal history of the sample, densities of glasses are always dependent upon the thermal history of the particular sample measured. Although the differences in density which result from changes in thermal history are not particularly large, they can be very important in certain applications, especially those requiring highly reproducible values of the refractive index of glasses.

Changes in density due to changes in thermal history are best explained by consideration of the volume/temperature diagram shown in Figure 7.4. A melt contracts as it is cooled. Once the temperature of the melt enters the transformation region, the relaxation time becomes significant as compared to the rate of cooling. If the melt is cooled rapidly, complete structural rearrangement to the state appropriate for each temperature cannot occur during the time the melt is actually at that temperature. Once the structural relaxation time exceeds the characteristic time for the experimental cooling rate, the structure becomes effectively fixed and does not change any further with decreasing temperature. The temperature which characterizes the structure of the equilibrium liquid which is frozen into the glass is known as the *fictive temperature*. Cooling of the melt at a slower rate will allow equilibrium to be maintained to a lower temperature, where the structure is more dense, before the structure become fixed. The fictive

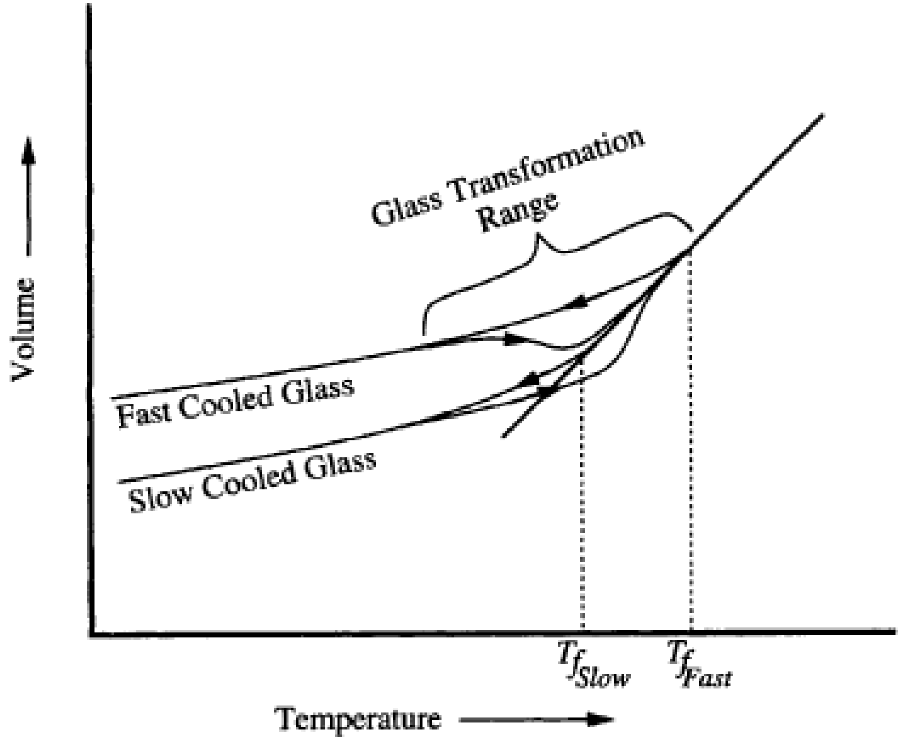

Figure 7.4 *Effect of temperature on the volume of glass forming melts*

temperature will be lower and the glass, after cooling through the elastic contraction region to room temperature, will be more dense.

Since the density of a glass is controlled by the cooling rate, a plot of density versus cooling rate can be generated. The density becomes

Density can also be altered by heat treatment at a specific temperature for times sufficient to allow equilibration of the structure to that appropriate for the treatment temperature. If we rapidly quench a melt, we obtain a glass sample which has a high fictive temperature and a low density. If we reheat this sample to a temperature within the transformation range, but below the original fictive temperature, the sample will readjust to the structure appropriate for the new temperature, become more dense, and will now be said to have a new fictive temperature. We can also slowly cool a melt, producing a low fictive

4.3 Effect of Phase Separation and Crystallization

Phase separation has very little effect on the bulk density of glasses. Since the measured density is a volume average of the densities of the phases present, the apparent density will vary smoothly as the relative volumes of the two phases vary. Plots of density versus composition expressed as weight fraction of one component for binary glass forming systems will always display a slight negative curvature within a region of phase separation. While such a region must occur for phase separated glasses, the existence of such a region is not proof that phase separation exists. The magnitude of the negative curvature is often so small that density plots are of little value in determining potential phase separation regions.

Crystallization can lead to much larger changes in density of glasses. If the density of the crystalline phase is significantly different from that of the residual glass remaining after crystallization, the density of the composite can vary over a large range. The density of commercial lithium aluminosilicate glass-ceramics, for example, is about 5% greater than the density of the glass before crystallization. The densities of

As a first approximation, the density, ρ, of a glass-ceramic is given by the expression:

$$\rho = \rho_x V_x + \rho_g V_g \tag{7.7}$$

where ρ_x and ρ_g are the densities of the crystalline and glassy phases, respectively, and V_x and V_g are the volume fractions of the same phases. This expression is usually correct to within ≈ 1% measured density. Deviations from this expression are often due to microcracks or to small concentrations of a third phase which is not included in the calculation.

4.5 Pressure Compaction

Glasses can also be permanently compacted by application of very high pressures. The density of vitreous silica can be increased by up to 15% by pressures in the 100 kbar range at room temperature, or by lower pressures at elevated temperatures. Densification is facilitated by a high shear component in the applied stress and by heating to within the glass transformation range. Annealing of these density increases occurs at temperatures well below the transformation range, but the kinetics of the annealing process are very complex.

5 THERMAL EXPANSION BEHAVIOR

The thermal expansion curve for a glass yields three important pieces of information: the thermal expansion coefficient, the glass transformation temperature, and the dilatometric softening temperature. The thermal expansion coefficient indicates the relation between the volume of a glass and its temperature. The glass transformation temperature indicates the onset of viscoelastic behavior, while the dilatometric softening temperature indicates the onset of flow under a modest load. Each of these properties is a strong function of glass composition. Lesser effects

5.1 Fundamentals of Thermal Expansion Behavior

Thermal expansion of close packed structures such as NaCl is the direct result of an increase in bond length with increasing temperature. The increase in bond length arises from the asymmetry of the potential energy versus interatomic distance curve of the Condon–Morse potential energy diagram (Figure 7.7). This curve results from the interaction of the repulsive and attraction terms of the interatomic potential, E_v, which is often expressed as:

$$E_v = -\frac{A}{R^n} + \frac{B}{R^m} \tag{7.8}$$

where A, B, n, and m are constants and R is the interatomic distance.

If the potential energy well were symmetric, the average interatomic distance would be independent of temperature even though the magnitude of the vibration amplitude would increase. Since the curve is asymmetric, however, the average interatomic spacing increases with increasing temperature. The degree of asymmetry is dependent upon the

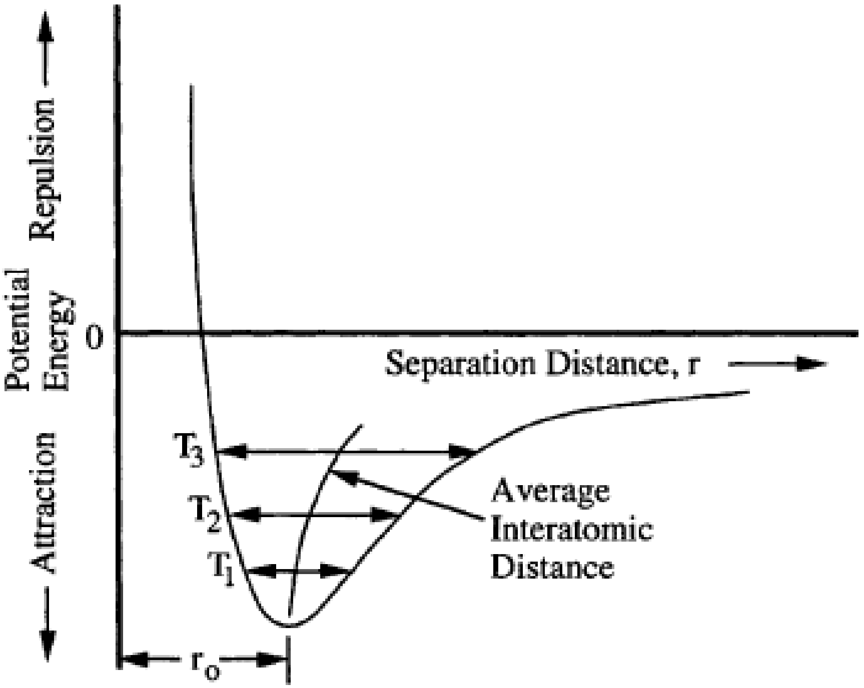

Figure 7.7 *Condon–Morse curve illustrating the cause of the thermal expansion of bonds*

value of n, which increases with bond strength from metallic to ionic to covalent bonds. As n increases, the curve becomes more symmetric and the thermal expansion coefficient decreases. Other factors also affect the symmetry of the bond. The creation of a non-bridging oxygen from a bridging oxygen increases the asymmetry of the bond to the neighboring silicon, or other network cation. Bonds between an anion and

Eventually, a temperature is reached where bond breaking begins to add still another factor to the overall thermal expansion of a structure. Bond breaking occurs at the melting point for crystalline materials, where a large, discontinuous increase in the thermal expansion coefficient usually occurs. The corresponding effect begins to occur at a measurable rate as we enter the glass transformation range during heating of a glass, where we find a gradual increase in the thermal expansion coefficient to the value of the equilibrium liquid. The intercept temperature of the extrapolated slopes from the expansion curve in the elastic and melt regions is usually used as the glass transformation temperature for thermal expansion data (Figure 7.8). As discussed earlier, the glass transformation temperature usually occurs when the viscosity is about 10^{12} Pa s.

the load. The temperature of maximum expansion is called the *dilatometric softening temperature*, or T_d (Figure 7.8). This temperature is an artifact of the dilatometric method used to measure the thermal expansion coefficient. As a result, it is slightly dependent upon the load applied by the push rod and the cross-sectional area of the sample, which, in combination, determine the stress on the sample. Values obtained from most laboratories, surprisingly, agree within a few degrees.

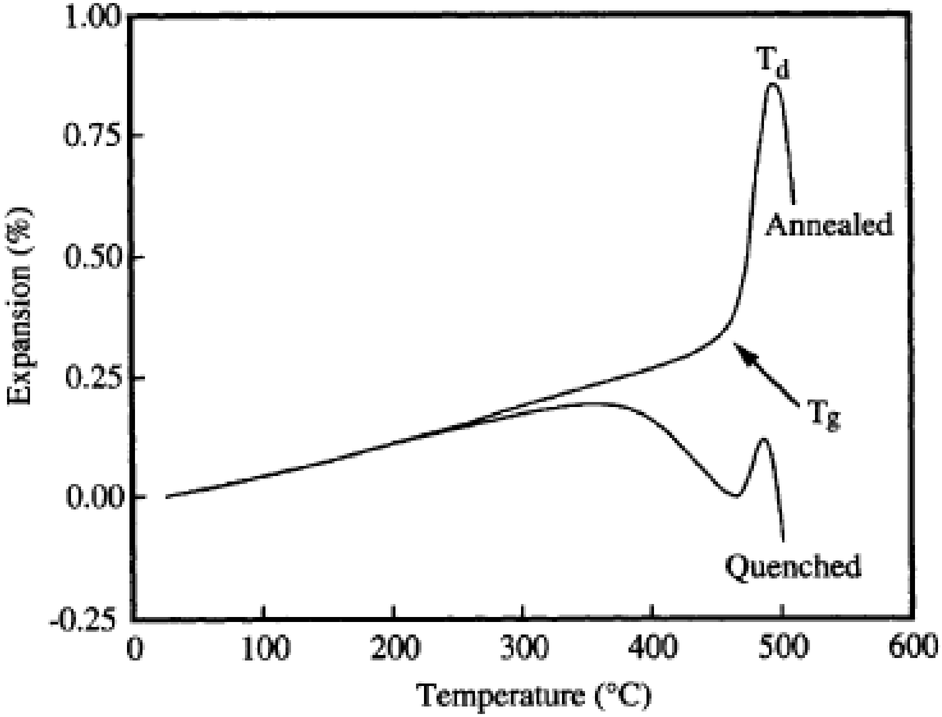

Figure 7.8 *Thermal expansion curves for annealed and quenched glasses*

5.2 Compositional Effects on Thermal Expansion Coefficients of Homogeneous Glasses

Thermal expansion coefficients of glasses, with few exceptions, increase with increasing temperature. The data can often be expressed over a wide temperature range for the elastic material by an equation of the form:

$$\alpha = \alpha_o + \alpha_1 T + \alpha_2 T^2 + \alpha_3 T^3 \tag{7.9}$$

where α_o, α_1, α_2, and α_3 are experimental constants.

Vitreous silica and a few other fully-linked network glasses display negative thermal expansion coefficients over a limited temperature range (Figure 7.9). These glasses are very useful for applications requiring insulating materials which are highly resistant to thermal shock and which maintain their dimensions during thermal cycling. The negative thermal expansion coefficients are believed to result from the ability of the network to absorb lattice expansion through bending of bonds into the empty interstices of the structure.

Vitreous boric oxide has a large, very temperature dependent thermal expansion coefficient in the range of 15 ppm K^{-1}. The large thermal expansion coefficient is due to the 2-dimensional nature of the structure of this glass, with weak bonds in the third dimension. Additions of alkali oxides initially decrease the thermal expansion coefficient (the *borate anomaly*), which passes through a minimum at ≈ 20 mol% alkali oxide and then increases monotonically to the glass formation limit for each system (Figure 7.10). The thermal expansion coefficient decreases in the order Cs > Rb > K > Na > Li, with a minimum value of ≈ 6 ppm K^{-1} for a $20Li_2O–80B_2O_3$ glass. The initial decrease in thermal expansion coefficient is primarily due to the conversion of boron from triangular to tetrahedral coordination, which increases the connectivity of the structure. The reversal in thermal expansion coefficient at higher alkali oxide concentrations is due to changes in the intermediate structural units and to the eventual onset of non-bridging oxygen formation with increasing alkali oxide content.

Although vitreous germania has a structure very similar to that of vitreous silica, its thermal expansion coefficient is approximately an order of magnitude larger. Gas diffusion studies indicate that the

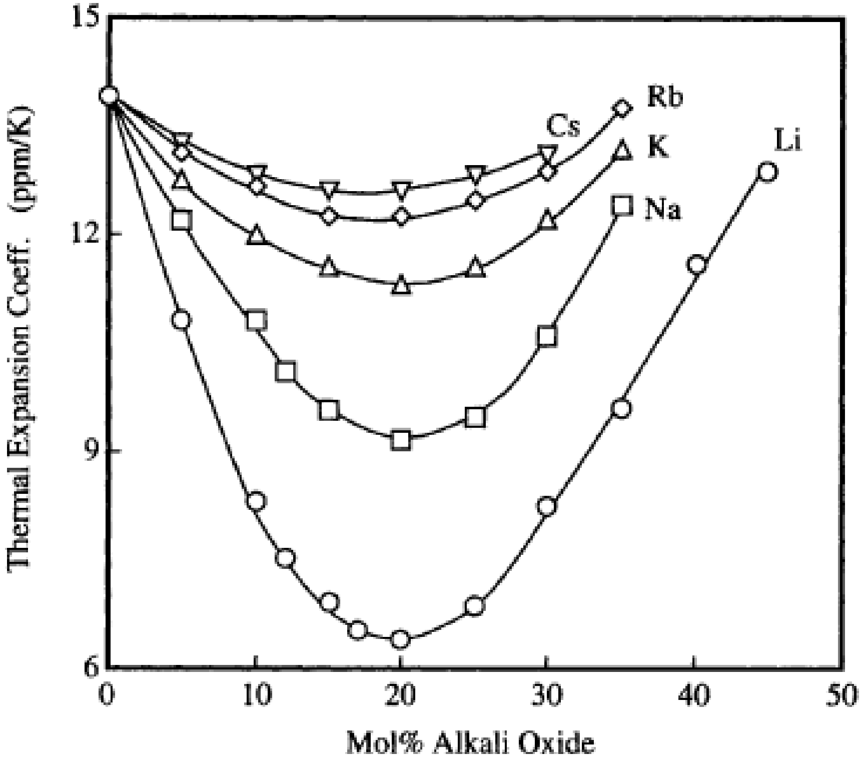

Figure 7.10 *Effect of composition on the thermal expansion coefficient of alkali borate glasses*

5.4 Thermal History Effects

Changes in fictive temperature have only a small effect on the thermal expansion coefficient for glasses at temperatures well below the transformation region. Heating a glass into the transformation region, however, allows relaxation to occur at rates which are comparable to the heating rates (3 to 5 K min^{-1}) used in these measurements. If we examine the curves shown in Figure 7.8, we find that reheating a quenched glass at a slower rate allows relaxation to occur before we reach the glass transformation temperature. The glass will actually contract at temperatures well below T_g. In extreme cases, the contraction can be so great that the sample will become shorter than its initial length. The determination of T_g from such a curve is no longer possible using the slope intercept method discussed previously.

5.5 Effect of Crystallization

Since the thermal expansion coefficient is a volume averaged function of the contributions of each of the phases present in a sample, formation of crystals with thermal expansion coefficients which are very different from the initial glass can radically alter the thermal expansion coefficient of the composite. Formation of crystals can also change the values of T_g and T_d by changing the composition of the residual glass, and by preventing deformation of the sample under the push-rod load.

Commercial lithium aluminosilicate glass-ceramics provide excellent examples of such behavior. The initial glass used for production of transparent cookware, for example, has a thermal expansion coefficient of ≈ 4 ppm K^{-1}, T_g ≈ 730 °C, and T_d ≈ 760 °C. After processing, the thermal expansion coefficient is ≈ 0.5 ppm K^{-1} and T_g and T_d can no longer be detected on an expansion curve below 1000 °C. Heat treatment results in the formation of a lithium aluminosilicate crystal which has a very low thermal expansion coefficient. Removal of lithium from the

The effect of crystallization on the thermal expansion behavior of a given glass also depends upon the identity of the crystalline phase formed. Heat treatment of the base glass used to produce one commercial lithium silicate glass-ceramic can yield either ≈ 33 vol% lithium metasilicate or ≈ 55 vol% lithium disilicate. Formation of lithium metasilicate will result in an increase in T_g from ≈ 480 to 620 °C, while T_d increases from 520 to 720 °C. Formation of lithium disilicate will yield a smaller increase in T_g to ≈ 570 °C, but a larger increase in T_d to ≈ 800 °C. The difference in composition of the residual glass due to

6 SUMMARY

Density, molar volume, and thermal expansion coefficients are determined by the structure and bonding within a glass, and are therefore strongly affected by changes in glass composition. Phase separation has little effect on these properties. The glass transformation and dilatometric softening temperatures are related to the viscosity of the melt, and are strongly affected by both the composition of the glass and by the microstructure of phase separated glasses. All of these properties are altered by crystallization.