

1.5 GLASS STRUCTURE

Glasses, or amorphous solids, lack long-range periodicity in their atomic arrangements. This is the single largest distinction between glasses and crystalline solids. However, not all types of glasses are structurally the same. While all—whether they are ceramics, semiconductors, or metals—are disordered over lengths greater than a few atomic separations, there are important differences between these materials in the level of order at the first few nearest-neighbor distances. We will see that oxide glasses and glassy covalent semiconductors (Si, Ge) have a number of structural similarities and can be described as *continuous random networks* based on the linkage of compact structural units (tetrahedra or triangles) similar to the nearest-neighbor coordinations in their crystalline counterparts. In contrast, glassy metals form in a *random close-packed* atomic array and lack distinct order even at the nearest-neighbor level. The structure of any glass can also vary significantly with its processing history.

To set a context for discussion of glass structure, we will first consider briefly the formation of glassy materials and a few of their properties. The subject of glass formation as related to the avoidance of crystallization is taken up in detail in Chapter 5.

Glass Formation

What causes a material to become glassy? Traditionally, glasses have been processed by cooling a liquid fast enough to prevent detectable crystallization. From this kinetic viewpoint, we can define glass formation as the *avoidance of crystallization*. The kinetics of glass formation are therefore those of crystal nucleation and growth, and in principle any liquid can be rendered glassy given a sufficiently rapid cooling rate. It is the difference in respective rates of crystallization that allows us to form many commercial oxide glasses by cooling at a leisurely rate of a few degrees per minute ($^{\circ}/\text{min}$), while metallic glasses must be quenched at more than 10^6 degrees per second ($^{\circ}/\text{sec}$). *Glass-ceramics* are commercially important ceramics with unique thermal shock and mechanical properties, made by controllably nucleating a very high density of crystals in a parent glass body. The processing and microstructure of glasses and glass ceramics are discussed in Chapter 5.

Glasses can also be made by a number of alternative processes, which have in common the aspect of consolidation at low temperatures to defeat crystallization. Condensation of a vapor onto a cold substrate is one method (*physical* or *chemical vapor deposition*), often used for the preparation of electronic thin-films (glassy and crystalline). Another is the gelation or precipitation of a disordered ceramic from liquid chemical solution (referred to as *sol-gel* processing), followed by densification into a glass. Irradiation and ion bombardment can be used to disorder initially crystalline materials and form a glass. Oxidation of silicon typically results in an amorphous film of SiO_2 , which has enormous technological importance as an insulating layer in silicon device technology. And, sometimes amor-

phous reaction products are formed between two crystalline solids when the equilibrium crystalline product cannot nucleate, in what are known as *solid-state amorphization reactions*. The structure and properties of glasses made by these techniques can differ substantially from those prepared from the melt; for instance, amorphous vapor-deposited silicon films undergo considerable structural rearrangement at temperatures well below those of crystallization or melting. Many of the novel processing techniques are restricted to the preparation of thin films of glass on a supporting substrate; some are not yet commercially important on a wide spread basis. For applications that require a monolithic body, the vast majority of glasses continue to be processed from the melt.

When we process glasses by cooling from the melt, the phase transformation from liquid to solid occurs at a *glass transition temperature* (T_g) that lies below the melting temperature T_m at which crystallization would otherwise take place. At T_g there is a transformation in physical properties from those of a liquid to those of a solid; one such property illustrated in Fig. 1.45 is the specific volume. The slope of this curve is directly related to the volume expansion coefficient α ($=\partial V/\partial T$ at constant composition and pressure). Above T_m one has a liquid; between T_m and T_g there exists a supercooled liquid (which despite references in the earlier literature is not a glass). At T_g , the change in slope in Fig. 1.45 shows a transition to a glassy state where structural rearrangements are no longer able

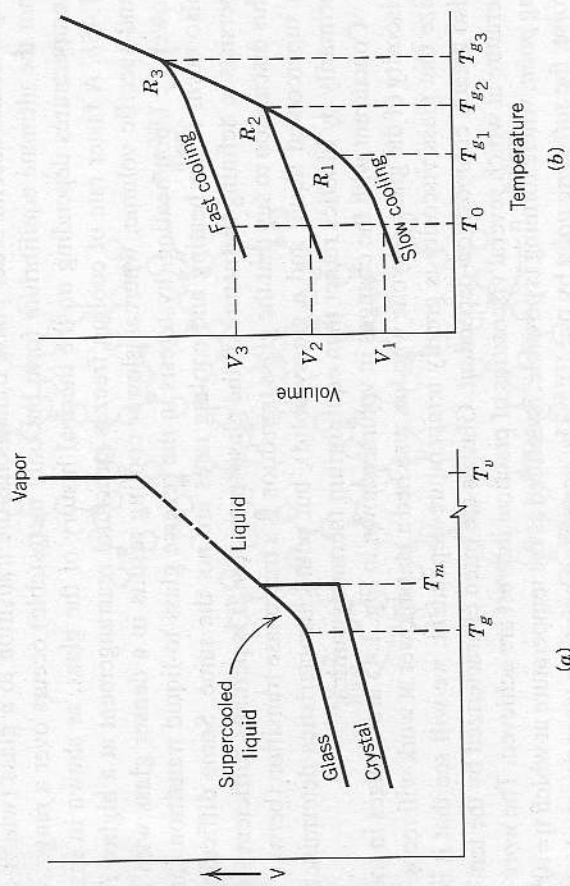


Fig. 1.45 (a) Volume-temperature relations for liquid, crystal, and glass phases. The transformation from a supercooled liquid to a glass occurs at the glass transition temperature, T_g . (b) Variation in T_g and specific volume of glass as a function of the cooling rate.

to take place on a reasonable time scale, and where the thermal expansivity and other properties become that of a solid. In most systems the specific volume of the glass is greater than the crystal (density is lower). According to the theory of D. Turnbull and M.H. Cohen, upon cooling of a liquid the *free volume*, defined as the volume available for molecules or polyhedra to maneuver without encountering strong interactions with their neighbors, decreases continuously until at the glass transition all free volume has been removed, leaving each molecule trapped in a local energy minimum from which all other positions are inaccessible.

We notice in Fig. 1.45 that the volume changes at crystallization and vaporization are discontinuous. Since volume is a first-derivative function of the free energy G (at constant composition x and temperature T):

$$V = \left(\frac{\partial G}{\partial P} \right)_{x,T}$$

the discontinuities in V at T_m and T_v define melting and vaporization as first-order phase transitions. In contrast, the change in V at T_g is continuous. The thermal expansivity α is a second-derivative function of G (first derivative of V), and since changes in α at T_g as well as other second-derivative functions such as heat capacity are fairly discontinuous, the glass transition has the appearance of a somewhat diffuse second-order phase transition. However, unlike equilibrium second-order phase transitions, the transition to a glass (which is not the ultimate equilibrium form but only metastable) occurs over a range of temperatures depending on the thermal history of the glass, as shown in Fig. 1.45b. A faster rate of cooling freezes structural rearrangement at a higher T_g and specific volume, whereas slower cooling results in a denser glass with a lower T_g . Upon heating, hysteresis in the reverse glass-to-liquid transition can also occur if the heating and cooling rates are not the same. Some difficulty persists in defining the nature of the glass transition. It is perhaps sufficient for this discussion to say that the glass transition is a true phase transition (between a supercooled liquid and a glassy solid), but with characteristics determined primarily by kinetics rather than equilibrium thermodynamics.

Concurrent with the changes in volume shown in Fig. 1.45 are changes in the viscosity of the glass. Anyone who has watched a glassblower at work will recognize that glass viscosity is greatly temperature-dependent; we will see that it is also greatly composition-dependent. Glasses are often characterized by the temperature at which several viscosities of practical interest are achieved. The *working point*, where forming is possible, is defined as the temperature at which $\eta=10^4$ Poise; the *softening point* by $\eta = 10^{7.6}$. The *annealing point* is a viscosity at which internal stresses can be substantially relieved in 15 minutes or so, and is defined as $\eta = 10^{3.4}$ Poise. The viscosity at the glass transition is 10^{13} - $10^{14.5}$ Poise for oxide glasses, and represents a limit above which structural rearrangements cannot take place at normal cooling rates.

Continuous Random Networks

Amorphous SiO_2 (fused silica) is the prototypical oxide glass. As in the crystalline silicates, directional covalent bonding and ionic bonding in accordance with Pauling's rules promote the formation of tetrahedral $(\text{SiO}_4)^{4-}$ basic structural units. Therefore, short-range order is identical in crystalline and glassy SiO_2 ; the coordination of anions around cations is four, and the O-Si-O bond angle within each tetrahedral unit is 109.5° . The O/Si ratio of 2 indicates that all four corners of each tetrahedra are interconnected in glassy SiO_2 , as is the case in the various crystalline phases of SiO_2 . However, it is possible for complete connectivity to be maintained without crystalline order; and this is the basis of the *continuous random network* structure first proposed by Zachariasen in 1932 (*J. Am. Chem. Soc.*, 54, 3841). In two dimensions, the continuous random network structure of an A_2B_3 glass is shown in Fig. 1.46.

Examining Fig. 1.46, and imagining the three-dimensional counterpart that is SiO_2 , we can identify three structural parameters at a medium range of order that allow us to distinguish between the crystalline and continuous random network amorphous structures. These are: (1) the angle of the Si-O-Si bond between tetra-

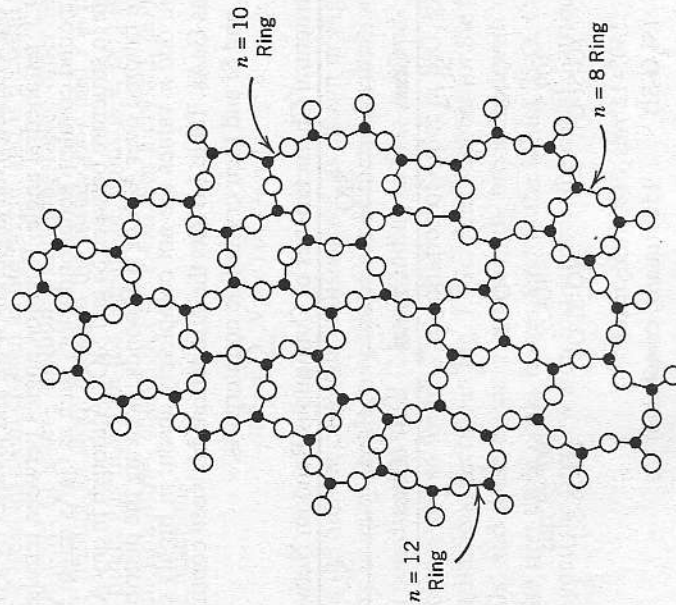


Fig. 1.46 Continuous random network model of an A_2B_3 glass. [From W. H. Zachariasen, *J. Am. Chem. Soc.*, 54, 3841 (1932).]