

Collage of Engineering
Materials Department

Third Class
Lecture (12)

GLASS

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6-2 Density and molar volume

The density ρ is the mass per unit volume (g/cm^3). If sample is free of bubbles, voids, or other defects, the calculated density is the true density of the material. If 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. 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:

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

Where V_m is the molar volume, MWt is the molecular weight of substance, and ρ is the true density of that substance. The molecular weight of a (25 Na₂O-75SiO₂) glass is equal to the sum of 0.25 times the molecular weight of Na₂O plus 0.75 times the molecular weight of SiO₂. If we use molecular weight of 61.981 for Na₂O 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. The density of a glass is a strong function of its composition. Crystallization of a glass can significantly alter the density, if the density of the crystalline phase is very different from that the residual glass. Densities of the common glass forming oxides are less than those of the corresponding crystalline forms of these compounds. If we calculate the free volume, V_f of the glass using the simple relationship:

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

Where V_x is the molar volume of the crystalline oxide form and V_g is the molar volume of the glass form, an obtained value of 0.27 or 27 %, for vitreous silica. 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.

If the networks formed by the primary glass forming oxides contain a large number of empty interstices, it must be possible to stuff a correspondingly large number of modifier ions into these interstices. Such a process would increase the mass of a substance without increasing its bulk volume, resulting in an increase in density. The addition of alkali ions to any of the common glass forming oxides results in an increase in density. 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. Shown in figure 17.

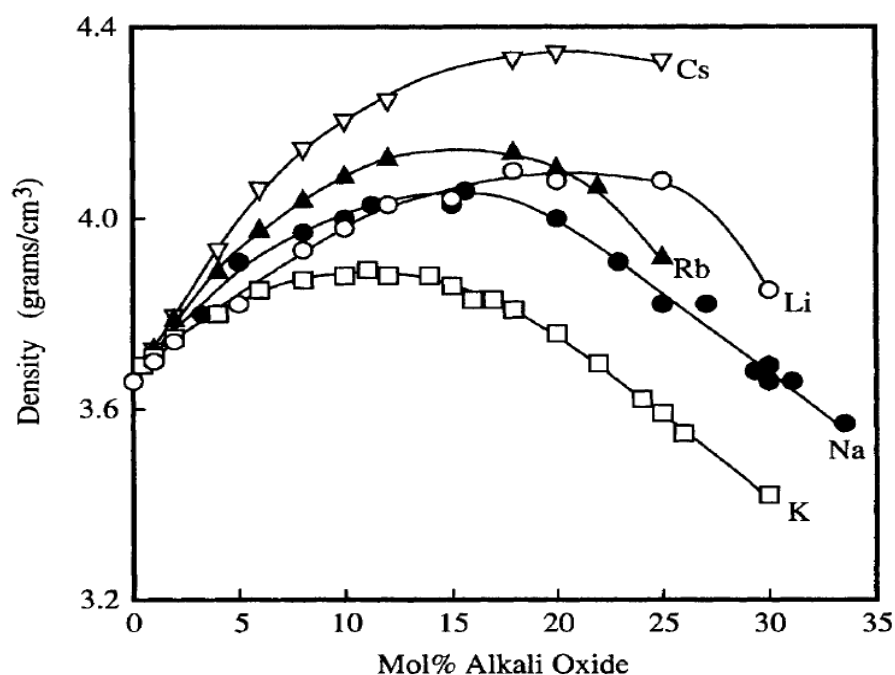


Figure (17) effect of composition on the density of alkali germanate glass

Glasses containing lithium are often more dense than those containing sodium or potassium. If potassium ion weights about 6 times as much as a lithium ion and both simply occupy interstices in an existing network.

The molar volumes in every case increase in order $\text{Li} < \text{Na} < \text{K} < \text{Rb} < \text{Cs}$. Additions of lithium or sodium to the network reduce the molar volume, implying that they cause shrinkage of the network. Potassium, rubidium, and cesium, on the other hand, increase the molar volume of glasses, implying that they force an increase in the volume of the structure. See in figure 18.

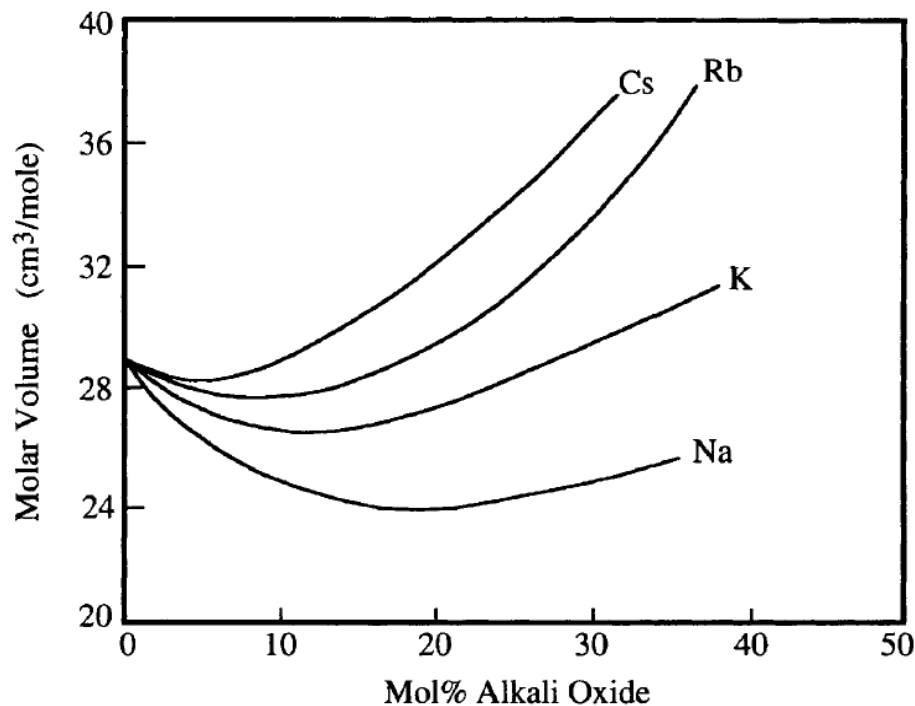


Figure 18 effect of composition on the molar volume of alkali germanate glass.

What happens when a melt of glass is cooled to room temperature? At very high temperature, where the melt is fluid, the melt consists of a mixture of modifier ions and various structural units of the network, which may be as small as the basic building block of the network, or which may consist of a few of these building blocks connected to form small discrete ions. At cooling, the network begins to form as the structural units become connected. If no alkali or other modifier ions were present, the network could form without hindrance from these ions. When modifier ions are present, the network must form around these ions. If the modifier ions are larger than the interstices which would form in their absence, the network will now contain a number of interstices which are larger than those of the modifier-free structure. If the

modifier ions are smaller, their attraction to the oxygen ions can lead to a decrease in size of the interstices. In the other world, the modifier ions are not simply filler for predetermined interstices, but modify the interstices formed, the relatively high mobility of the modifier ions on the time scale of network relaxation as the melt approaches the transformation range allows each modifier ion to influence the size of several interstices. As a result, large ions such as cesium may increase the free volume of the network, while small, higher field strength ions such as lithium can decrease the free volume.

The interstices in glass act as sieves through which mass can move. Thus, in glasses, conduction of charge occurs predominantly by those ions that can move through the interstices. Network modifying ions, particularly the alkali ions, invariably carry the bulk of the charge conduction. Therefore, properties that depend upon motion of ions through the interstices would clearly be enhanced by how open the glass structure is.

Thus, the migration of an inert gas atom such as He is expected to be much faster through silica glass than through a soda lime silicate, because the network modifying cation Na^+ and Ca^+ act to block the available pathways in the silica structure. A larger cation in the interstice plays a more effective blocking role than a smaller modifying cation. In fact, the thermally activated properties that depend upon an atomic/ ionic jump from one site to another should display a distribution of activation energies, because the separation distance of the sites in glass is distributed.

Due to the open structure of glasses, application of an outside pressure drives the individual smaller structure units to rearrange in such a way that a better filling of space occurs with a higher density. This is accompanied by a decrease of the average Si-O-Si angle of silica glass.