1 INTRODUCTION

Although not normally discussed as a component of individual glasses, it should be recognized that all glasses contain chemically bound water. This water can occur in the form of hydroxyl bonded to the basic building blocks of the structure, or as molecular water dispersed in the interstices of the network. The concentration of water can range from parts per billion for the best vitreous silica optical fiber, to hundreds of parts per million for typical commercial glasses, to many percent for glasses found in nature. The presence of water is easily detected in the infrared spectra of glasses.

Since water has a larger effect on some properties of glasses per unit of concentration than any other component, it deserves discussion as a separate chapter of this book. This chapter will first discuss the spectral detection of water in glasses and the methods used to vary the water content of glasses. The next section of the chapter will consider the experimental methods for measuring diffusion and solubility of water in glasses and melts, and the effect of composition and other factors on the results. The final portion of the chapter will present data illustrating the large effect of water on certain properties of glasses.
2 EFFECT OF WATER ON THE INFRARED SPECTRA

The presence of hydroxyl and molecular water in glasses is detected by measurement of the infrared spectrum between 2000 and 4000 cm\(^{-1}\).

2.1 Network Glasses

Virtually all oxide glasses contain hydroxyl in various forms, while other molecular species may or may not be present. The primary absorption band due to Si–OH bonds occurs at 3673 cm\(^{-1}\) for vitreous silica (Figure 11.1).

![Infrared spectra](image)

Figure 11.1. Infrared spectra of vitreous silica, a commercial soda–lime–silica glass and a sodium borosilicate glass (curves are offset for clarity)
2.2 Other Silicate Glasses

Addition of alkali oxide to silica results in the formation of new bands due to hydroxyl as well as a shift in the position of the fundamental band toward the infrared. Hydroxyl bands are found at 3650 to 3450, 3000 to 2600, and 2350 cm\(^{-1}\) for common sodium silicate and soda–lime–silica glasses (Figure 11.1).

The hydroxyl spectra of alkali borosilicate glasses, which are often phase separated, with silica-rich and alkali borate-rich regions, are also very different from those of glasses containing large quantities of non-bridging oxygens, as is also shown in Figure 11.1. The hydroxyl band is very broad and typically occurs at frequencies around 3600 cm\(^{-1}\). It has been shown that the hydroxyl in phase separated glasses tends to concentrate in the modifier-rich glassy phase.

In addition to hydroxyl, molecular water can also be found in large concentrations in glasses formed under high pressures of water vapor. Commercial glasses and those produced by routine methods in the laboratory contain very little molecular water. On the other hand, most naturally occurring glasses, e.g., basalt and obsidian, contain large concentrations of molecular water. In general, glasses containing less than 1 wt% total water will contain primarily hydroxyl. The concentration of hydroxyl maximizes in glasses at about 2 wt%, after which all additional water is found in the molecular form.
2.3 Silane in Glasses

Glasses can also contain bound hydrogen in the form of Si–H units. The fundamental vibration for Si–H occurs at 2250 cm\(^{-1}\) for vitreous silica. This absorption band is much sharper than those due to hydroxyl. Since this band overlaps another band at 2260 cm\(^{-1}\), which is due to an overtone of a fundamental Si–O–Si vibration, the spectrum of an otherwise identical glass known to be free of Si–H must be subtracted from that of the glass suspected of containing Si–H before the band at 2250 cm\(^{-1}\) can be detected.
3 FORMATION OF HYDROXYL

Hydroxyl can be formed in glasses by many methods. The most common form of hydroxyl stems from melting in the presence of water vapor, which is always present at some level in the atmosphere, and thus occurs for all commercial and laboratory melts. Hydroxyl, accompanied by Si–H, is produced by melting in atmospheres containing a significant amount of hydrogen. Irradiation by any high energy source can form Si–OH and Si–H in glasses containing dissolved molecular hydrogen.

3.1 Reaction with Water

Formation of hydroxyl by reaction with water vapor can be described by the reaction:

$$\text{Si–O–Si} + \text{H}_2\text{O} = \text{Si–OH} + \text{OH–Si}$$  \hspace{1cm} (11.1)

and by analogous reactions for other glass forming oxides. Hydroxyl formed by reaction of water vapor with the melt is very stable. The hydroxyl content of glasses can be reduced by melting in atmospheres containing very low partial pressures of water vapor, or by long heat treatments in very dry atmospheres, or in vacuum at temperatures within the glass transformation range. Addition of halides to the batch has also been found to be an effective way to reduce the amount of hydroxyl formed during melting. The halides react with the protons to form species such as HF or HCl, which are very volatile and are rapidly released from the melt as a corrosive vapor.
3.2 Reaction with Hydrogen

Hydroxyl can also be formed by reaction with H₂, as described by the reaction:

\[ \text{Si–O–Si} + \text{H}_2 = \text{Si–OH} + \text{H–Si} \]  \hspace{1cm} (11.2)

The hydroxyl and hydride groups formed by these reactions are less stable than those formed by reaction with water molecules and can be removed at lower temperatures. The reaction described by Eq. 11.2 can be driven either thermally during melting in an atmosphere containing H₂, or by irradiation at room temperature of glasses containing dissolved hydrogen. The thermal stability of the species formed is quite different, with a much lower temperature required for removal of the hydroxyl and hydride formed during irradiation, than for that formed by thermally driven reactions.
4 DIFFUSION AND SOLUBILITY OF WATER IN GLASSES AND MELTS

Diffusion and solubility of water in melts was first studied in detail by Scholze and co-workers around 1960. Very little additional work was done in this area until recent years, when the replacement of air by pure oxygen in the firing of glass tanks resulted in a considerable increase in the hydroxyl content of commercial glasses. Replacement of air by oxygen for combustion reduces the formation of nitrous oxides, and thus reduces the air pollution created by the glass manufacturing process.

4.1 Water Diffusion Measurements in Glasses

Almost all water diffusion measurements in glasses have been made by removing the hydroxyl created during the initial production of the glass. A thin, polished plate of the glass is heated in vacuum at temperatures near or within the glass transformation range. The relative concentration of hydroxyl is determined as a function of treatment time by measuring the height of an infrared band due to hydroxyl. It is usually assumed that all of the hydroxyl will be removed if sufficient time is devoted to heat treatment of the sample. The fraction removed is determined at each treatment time by dividing the height of the infrared band by the original height of the band. This “fraction of reaction” is plotted against the square root of the treatment time, divided by the thickness of the sample (Figure 11.2). The diffusivity, $D$, is calculated from the initial slope, $R$, of a best fit curve through the data by use of the expression:

$$D = \frac{\pi R^2}{16}$$

(11.3)
4.2 Water Diffusion Measurements in Melts

Water diffusion measurements in melts are carried out in a similar manner to those in glasses. In this case, however, the melt must be contained in a crucible. As a result, diffusion can only occur from one surface instead of from 2 surfaces as is the case for plates. Eq. 11.3 is altered by replacing the factor of 16 by a factor of 4:

\[ D = \frac{\pi R^2}{4} \]  

(11.4)
4.3 Water Solubility Measurements

Water solubility measurements can be made in a number of ways. Most studies are based on infrared spectroscopy and the Beer-Lambert Law:

\[ A = \varepsilon c L \]  \hspace{1cm} (11.5)

where \( A \) is the absorption above background, \( c \) is the concentration of water in the sample, \( L \) is the sample thickness, and \( \varepsilon \) is the extinction coefficient for water in that specific glass.
4.4 Effect of Composition on Water Diffusion and Solubility

It has been proposed that water solubility is directly related to the “basicity” of melts. For silicate melts, the basicity is essentially a measure of the concentration of non-bridging oxygens in the structure. Since a melt is highly disrupted, the concept of bridging and non-bridging oxygens is somewhat questionable. In general, however, it is found that the solubility of water increases with increasing alkali oxide concentration in silicate melts. Increasing alkaline earth oxide contents will increase water solubility if the oxide replaces silica, but will decrease water solubility if an alkaline earth oxide replaces an alkali oxide. In alkali borate and germanate melts, on the other hand, addition of alkali oxides decreases the solubility of water, even though the melts become more basic as the acidic glass former oxide is replaced by the modifier oxide (Figure 11.4).
Figure 11.4. Effect of composition on the solubility of water in sodium silicate, borate, and germanate melts.
5 EFFECT OF WATER ON PROPERTIES OF GLASSES

On an atom-for-atom basis, water has a greater effect on certain properties of glasses than any other oxide. It has been shown that water alters the density, refractive index, and dielectric constant of glasses. Less convincing evidence exists for a significant effect of water on elastic moduli and thermal expansion coefficients. The effect of water on the glass transformation temperature, viscosity, and relaxation rates, however, is surprisingly large, with changes of as much as 40 K for $T_g$ of otherwise identical glasses, melted under atmospheres containing different amounts of water vapor. The effect of water on the infrared spectrum, as discussed above, has also proven to be very important in the application of glasses for infrared transmitting materials such as optical fibers for telecommunication systems, where absorption due to hydroxyl is extremely detrimental to the use of these fibers.
5.1 Glass Transformation Temperature and Viscosity

The effect of water concentration on $T_g$ and isothermal viscosity is most evident for the glass former oxides. Commercial vitreous silica is produced with water contents ranging from $<1$ to $>600$ wtppm of $\text{H}_2\text{O}$. The $T_g$ of these glasses decreases from $\approx 1200^\circ \text{C}$ to only $1060^\circ \text{C}$ over this range. The $T_g$ of vitreous boric oxide ranges from $\approx 200^\circ \text{C}$ for glasses containing as much as 1 wt% $\text{H}_2\text{O}$, to over $300^\circ \text{C}$ for the driest glasses, which contain $<100$ wtppm $\text{H}_2\text{O}$. The water content of vitreous boric oxide covers a much wider range than that of vitreous silica, and is highly dependent on the raw material used to produce the glass. Use of boric acid, which is $\approx 50\%$ water, results in a very “wet” glass, while use of anhydrous boric oxide, combined with melting under a low humidity atmosphere, produces a very dry glass.

The effect of water on $T_g$ and viscosity is smaller, but still very significant for other glasses. The $T_g$ of soda–lime–silica glasses, for example, decreases by $\approx 4$ K for every 100 wtppm of water in the glass.
to 50 K can be found for the same bulk glass. The effects of water concentration on the $T_g$ of a commercial float glass, a lithium diborate glass, and a sodium trisilicate glass are shown in Figure 11.5. While the slopes of the lines are very different, the decrease in $T_g$ with increasing water concentration is evident for each glass. The higher solubility of water in borate glasses allows preparation of glasses with a much wider range of concentrations of water content than is possible for silicate glasses.

The $T_g$ of a commercial soda–lime–silicate glass which was melted in an older, air-fuel fired tank, which contains about 350 wtppm of water, is typically 5 to 7 K greater than that of the same glass produced by the same manufacturer in an oxygen-fuel tank.

The large effect of hydroxyl on viscosity and $T_g$ is attributed to the formation of additional non-bridging species in the network, i.e., the bridging oxygens are converted to non-bridging hydroxyls. The reduction in the connectivity of the network allows relaxation of the structure and motion of the flow units to occur at lower temperatures.
5.2 Density and Refractive Index

The effect of water content on density and refractive index of glasses is much smaller than for $T_g$ and viscosity. The density of vitreous silica decreases by 0.003 g cm$^{-3}$, while the refractive index decreases by 0.0001 for an increase of 600 wtppm of water, for glasses with identical fictive temperatures.

Limited data for alkali silicate glasses indicate that water has the opposite effect on density and refractive index from that found for vitreous silica, with an increase of 0.001 g cm$^{-3}$ in density and an increase of 0.0006 in refractive index for an increase of 1000 wtppm in water concentration, for a typical soda–lime–silica glass.
5.3 Other Properties

A very small increase of 0.05 ppm K$^{-1}$ has been reported for the thermal expansion coefficient of vitreous silica for an increase of several hundred wtppm of water. The thermal expansion coefficients of sodium trisilicate glasses and commercial soda–lime–silica glasses containing different amounts of water do not change by a detectable amount. The heat capacity of vitreous silica at 700 °C is reduced by 1.6% by a change in water concentration of 600 wtppm.

6 SUMMARY

All oxide glasses contain chemically bound water, usually in the form of hydroxyl. The effects of water content on the infrared spectrum, glass transformation temperature, and melt viscosity are very important in a number of commercial applications. Variations in reported values for $T_g$ of glasses of supposedly the same composition are probably due to variations in water content, which should be specified in any work dealing with the properties which are particularly sensitive to water concentration.