1 INTRODUCTION

Glasses are among the few solids which transmit light in the visible region of the spectrum. Glasses provide light in our homes through windows and electric lamps. They provide the basic elements of virtually all optical instruments. The worldwide telecommunication system is based on the transmission of light via optical waveguides. The esthetic appeal of fine glassware and crystal chandeliers stems from the high refractive index and birefringence provided by lead oxide, while the magnificent windows of many cathedrals exist only because of the brilliant colors which can be obtained in glasses.

The optical properties of glasses can be subdivided into three categories. First, many applications of glasses are based on bulk optical properties such as refractive index and optical dispersion. Other properties, including color, are based on optical effects which are strong functions of wavelength. Finally, modern glass technology increasingly relies on the application of non-traditional optical effects such as photosensitivity, photochromism, light scattering, Faraday rotation, and a host of others.
2 BULK OPTICAL PROPERTIES

The history of optical science closely parallels the history of the development of optical glasses. Development of early telescopes and microscopes immediately forced a search for new optical glasses with appropriate refractive index and optical dispersion characteristics. It can be argued that the development of modern astronomy, biology, and medical science were controlled by the ability of glass makers to develop glasses with the appropriate optical properties.

2.1 Refractive Index

The refractive index remains the most measured optical property of glasses, as well as the most basic optical property for determination of the appropriate glass for many applications. The refractive index of any material is defined as the ratio of the velocity of light in a vacuum divided by the velocity of light in a medium. This ratio can be measured by application of Snell’s law, which states that the refractive index, \( n \), is given by the expression:

\[
n = \frac{\sin \Theta_i}{\sin \Theta_r}
\]

(10.1)

where \( \Theta_i \) is the angle of incidence and \( \Theta_r \) is the angle of refraction for a beam of light striking the surface of a material. The refractive index can
Total internal reflection

Cladding has lower refractive index

Core has higher refractive index
The refractive index of a glass is determined by the interaction of light with the electrons of the constituent atoms of the glass. Increases in either electron density or polarizability of the ions increases the refractive index. As a result, low indices are found for glasses containing only low atomic number ions, which have both low electron densities and low polarizabilities. Glasses based on BeF$_2$ have refractive indices in the order of 1.27, while vitreous silica and vitreous boric oxide have refractive indices of about 1.458. At the other extreme, glasses with high lead, bismuth, or thallium contents may have refractive indices ranging from 2.0 to 2.5.

Since a majority of the ions in any glass are usually anions, the contribution to the refractive index from the anions is very important. Replacement of fluorine by more polarizable oxygen ions, or by other halides, increases the refractive index. Conversely, partial replacement
example, reduces the refractive index. Since non-bridging oxygens are more polarizable than bridging oxygens, compositional changes which result in the formation of non-bridging oxygens increase the refractive index of glasses, while changes in composition which reduce the non-bridging oxygen concentration can reduce the refractive index. The refractive indices of alkali silicate glasses (Figure 10.1) thus increase with increasing alkali oxide concentration, while replacement of alkali oxides by alumina, which reduces the non-bridging oxygen concentration, can cause a reduction in the refractive index.

Figure 10.1 Effect of composition on the refractive index of alkali silicate glasses
The density of a glass also plays a role in controlling the refractive index. Decreases in fictive temperature, which increase the density of most glasses, increase the refractive index. Since the fictive temperature is determined by the cooling rate through the glass transformation region, the refractive index is found to increase with decreasing cooling rate. This effect can be very important for optical applications, where

Thermal expansion of glasses can result in either an increase or a decrease in the refractive index. The density of a glass will decrease if it expands upon heating, which should decrease the refractive index. The polarizability of the ions, however, increases with temperature, which increases the refractive index and may therefore offset the effect of the decreasing density. Glasses with high thermal expansion coefficients
2.2 Molar and Ionic Refractivity

The *molar refractivity* is directly proportional to the polarizabilities of the constituent ions of a glass. It can be shown that the molar refractivity, $R_m$, is given by the expression:

$$R_m = V_m \left( \frac{n^2 - 1}{n^2 + 2} \right)$$  \hspace{1cm} (10.2)

where $V_m$ is the *molar volume* of the glass and $n$ is the refractive index at the wavelength of measurement. The molar volume is equal to the molecular weight of the glass divided by its density.

The molar refractivity of a compound can be calculated from the contributions of each of the constituent ions. The molar refractivity for the compound $A_xB_y$, for example, is given by the sum of the *ionic refractivities* of the constituent ions, $R_i$, times their concentration in the compound, or, in this case:

$$R_m = xR_A + yR_B$$  \hspace{1cm} (10.3)

Since the ionic refractivity depends on the polarizability of the ion, large values are found for the large, low field strength ions such as $\text{Tl}^+$ and $\text{Pb}^{2+}$. Variations in the ionic refractivity explain many of the major trends in the refractive index of glasses.
The ionic refractivity of oxygen depends upon its role in the glass structure, so that the values for bridging and non-bridging oxygens are not identical. Furthermore, the ionic refractivity of oxygen ions depends on the nature of the associated cations. As a result, one can only use ionic refractivities as a guideline to choice of ions for altering the refractive index of oxide glasses, and not for quantitative calculations.

2.3 Dispersion

The variation in index with wavelength, known as optical dispersion or simply as dispersion, is critical in the control of chromatic aberration of optical lenses. Ideally, dispersion is described by the entire curve of
3 ULTRAVIOLET ABSORPTION

Even transparent, colorless glasses cannot transmit radiation at wavelengths beyond their inherent ultraviolet edge. This frequency is believed to be due to the transition of a valance electron of a network anion to an excited state. Conversion of a network anion from the bridging state to a non-bridging state will lower the energy required for the electronic excitation, and shift the ultraviolet edge to lower frequencies. The addition of alkali oxides to silica, therefore, results in a shift of the ultraviolet edge toward the visible region of the spectrum. Since initial additions of alkali oxides to boric oxide result in conversion of boron from 3- to 4-fold coordination, thus strengthening the network bonds, the ultraviolet edge does not shift toward the visible. Once the concentration of alkali oxide becomes sufficient to produce non-bridging oxygens, the expected shift of the edge toward the visible with increasing alkali oxide content is observed.

4 VISIBLE ABSORPTION

Absorption in the visible is perceived as color. A number of mechanisms exist for the creation of color in glasses. The most important commercial colored glasses contain either 3d transition metal ions or 4f rare earth (lanthanide) ions, where the coloration arises from the so-called ligand field effect. Other sources of color include the formation of metal or semi-conductor colloidal particles, optical defects induced by solarization or radiation, and charge transfer bands in the visible region of the spectrum.
4.1 Ligand Field Coloration of Glasses

Coloration of glasses by 3d transition metals ions is due to electronic transitions between normally degenerate energy levels of d-electrons. Since a detailed description of the mechanism leading to these electronic transitions (called ligand field or crystal field theory) can be found in many places, only a brief qualitative discussion will be provided here.

The 3d electronic levels are identical in energy for free ions. However, when a transition metal ion is surrounded by a few anions, called ligands, as in a crystal or glass, the interaction of the electric fields causes a small splitting of the energy levels. The magnitude of this splitting is a function of the field strength, number, and geometric arrangement of the neighboring anions. The number of different levels formed is a function of the electronic configuration and coordination number of the cation. Since the energy differences which commonly result for 3d transition metal ions from ligand fields are in the range of 1 to 3 eV, the absorption of photons by electronic transitions between split 3d levels results in visible coloration.

Similar arguments apply to the 4f electronic levels of the rare earth ions, where splitting of the 4f levels also produces absorption bands in the visible. Differences in the nature of the 3d and 4f ions result in less
4.2 Amber Glass

Many glass containers have a brownish color popularly called “beer-bottle brown.” This particular color occurs in glasses containing both iron and sulfur. Carbon is usually added to the batch to provide a reducing agent to insure the presence of sulfide ions. One model suggests that the coloration is due to the presence of a ferric ion in tetrahedral coordination with three \( \text{O}^{2-} \) and one \( \text{S}^{2-} \) ions. The optical absorption is due to a charge transfer process.

4.3 Colloidal Metal Colors

The red color produced in many glasses containing gold, known as gold-ruby glasses, is due to the presence of very fine colloidal gold particles. The color is not due to light scattering, but rather to absorption by the particles, which cause an intense optical absorption band at about 530 nm. Doremus has calculated the shape and position of this band by assuming that the particles are spherical and using the optical properties of gold. He suggests that this band can be considered as a plasma resonance band, where the free electrons in the particles are treated as a bounded plasma. A similar absorption band, attributed to an identical mechanism, at 410 nm is obtained for glasses containing colloidal silver (Figure 10.3). The shift in band position results in a strong yellow coloration, which is called silver-yellow or silver stain.

A somewhat less esthetically pleasing red color can be produced in glasses containing copper. The absorption band due to copper occurs at 565 nm for these glasses and is similar in shape to those for gold and silver. While the red color of these glasses is usually attributed to copper colloids, others have proposed that the color is due to colloidal crystals of \( \text{Cu}_2\text{O} \). Since both metallic copper and \( \text{Cu}_2\text{O} \) are often found in copper-ruby glasses, it is possible that the color arises from a combination of these species. Although the solubility of both gold and silver in
Figure 10.3  Optical absorption spectrum for a glass containing silver colloids.  (Data supplied by C. E. Heckle)
4.6 Solarization

Coloration of glasses by exposure to sunlight is known as solarization. Although some of the defects produced by higher energy radiation can also be produced by ultraviolet radiation, the classic solarization of glasses is due to a radiation-induced change in the valence of manganese, via the reaction:

\[ \text{Mn}^{2+} + \text{Fe}^{3+} + \text{photon} = \text{Mn}^{3+} + \text{Fe}^{2+} \]  \hspace{1cm} (10.10)

Many years ago, manganese was frequently added to glasses to serve as a "decolorizer" for iron-induced optical absorption. Since this practice is no longer common, modern glasses do not produce the deep purple color characteristic of Mn\(^{3+}\) ions after long term exposure to sunlight. While less common, other pairs of ions, including Mn–As, Fe–As, and several couples involving cerium, can also produce optical absorption changes due to solarization. Solarization of modern glasses usually produces brown shades similar to those produced by higher energy irradiation.

5 INFRARED ABSORPTION

Absorption of light in the ultraviolet and visible regions of the spectrum is due to electronic transitions. While there are some lower energy electronic transitions in the infrared region of the spectrum, most optical absorptions in this region in glasses are due to vibrational transitions.
Frequency is the more fundamental parameter, in that it is directly related to the source of the radiation, the energy difference between the atomic or molecular levels. However there is no direct way of measuring frequencies as high as that of light. In contrast the measurement of wavelength is possible to a very high accuracy. Therefore all spectral measurements are made in terms of wavelength.

Light is a particular form of electro-magnetic radiation which affects the retina of the human eye to give sight. The retina is sensitive to a relatively narrow range of wavelength 400 to 700 nm.
The term electro-magnetic radiation covers a wide range of wave phenomena, from radio waves, through light, to gamma rays. Electromagnetic radiation is a transverse wave phenomenon and the common parameter frequency is the number of waves which pass a given point in space per second.

The wave length of the radiation is the distance between successive wave maxima.

\[
\text{frequency} = \text{velocity} / \text{wavelength} \\
\text{(Hertz, 1/sec)} \quad \text{(m/sec)} \quad \text{(m (nm))}
\]
The visible spectrum is the portion of the electromagnetic spectrum that is visible to (can be detected by) the human eye.

Eye sensitivity

<table>
<thead>
<tr>
<th>Wavelength (nm)</th>
<th>Color</th>
</tr>
</thead>
<tbody>
<tr>
<td>400-450</td>
<td>violet</td>
</tr>
<tr>
<td>450-500</td>
<td>blue + indigo blue</td>
</tr>
<tr>
<td>500-570</td>
<td>green</td>
</tr>
<tr>
<td>570-590</td>
<td>yellow</td>
</tr>
<tr>
<td>590-610</td>
<td>orange</td>
</tr>
<tr>
<td>610-700</td>
<td>red</td>
</tr>
</tbody>
</table>
Refractive index depends on:

a-) the type of incident light (wavelength and frequency)
b-) the structure of the material (medium)

<table>
<thead>
<tr>
<th></th>
<th>density (g/cm³)</th>
<th>refractive index</th>
</tr>
</thead>
<tbody>
<tr>
<td>Borosilicate glass</td>
<td>2.30</td>
<td>1.47</td>
</tr>
<tr>
<td>Soda-lime silicate glass</td>
<td>2.50</td>
<td>1.50</td>
</tr>
<tr>
<td>PbO glass (Crystal glass)</td>
<td>2.55</td>
<td>1.55</td>
</tr>
</tbody>
</table>
Speed and angle of light changes as the medium changes. It slows down if the density of the new medium is higher than the first one.

\[ \eta, \text{ refractive index} = \frac{\sin \alpha}{\sin \beta} \]

\( \alpha: \) angle of incidence
\( \beta: \) angle of refraction
Objects do not generate light, but they absorb or reflect it.
The change of refractive index due to the change in wavelength is called as “dispersion”. So dispersion has a wavelength dependant nature. Media having such a property are termed “dispersive media”. Glass is a dispersive medium.

In 1670, Sir Isaac Newton discovered that the sunshine (white light) is made up a combination of many colors.
When radiation strikes the surface of a body:

- it is either transmitted, or
- absorbed, or
- reflected.

The sum of the reflectance $R$, the transmittance $T$, and the absorptance $A$ is unity.

\[ R + T + A = 1 \]

$R$: the ratio of reflected light (reflectance)
$T$: the ratio of transmitted light (transmittance)
$A$: the ratio of absorbed light (absorptance)
The sum of the reflectance $R$, the transmittance $T$, and the absorptance $A$ is unity.
- Our most important energy source is light, and the entire spectrum of colours is derived from light. Sunlight, which contains all the wavelengths, consists of the entire electromagnetic spectrum.

- Color is a combination of different effects occurring in the human eye, generated by the light at various wavelengths of visible range.

- We know that each colour found in the visible light spectrum has its own wavelength and its own frequency, which produces a specific energy. Light consists of the seven colour energies: Red, Orange, Yellow, Green, Blue, Indigo, and Violet.
Each color has a different wavelength; blues and violets have shorter wavelengths, greens in the middle of the visible range and reds, oranges and yellows have longer wavelengths. When colored wavelengths fall on the retina, the nervous system and the brain interpret the signals as color.
Iron Oxide

- Iron oxide exists in two oxidation levels in glass.
- The color caused by iron oxide depends on the oxidation level of iron.
- $\text{Fe}^{+2}$ has a strong absorption at 1050 nm wavelength near IR region.
- $\text{Fe}^{+3}$ has an absorption at UV region of the spectrum and its absorption reaches to visible region.

This absorption band has a maximum around 380 nm, and continues through visible region until 430-440nm.

Bluish green

This absorption band continues until 500nm.
Coloring ions in glass

1- Transition elements
   Fe
   Cr
   Co
   Mn
   Cu
   Ni
   V

2- Rare earth elements
   Ce
   Nd
   Pr
   Er
   Ho

3- Colloidal metallic particles
   Cu
   Au
   Ag
Chromium Oxide

- Chromium oxide exists in two oxidation levels in glass.
- The color caused by chromium oxide depends on the oxidation level of chromium.
  - $\text{Cr}^{3+}$, has a strong absorption at $450-650 \text{ nm}$.
  - $\text{Cr}^{6+}$, has an absorption at $370 \text{ nm}$.
Emerald green (coloring with \( \text{Cr}_2\text{O}_3 \))

\[ \text{Cr}_2\text{O}_3 \rightarrow \text{Cr}^{+3} \text{ (emerald green)} \]
\[ \text{Cr}_2\text{O}_3 \rightarrow \text{Cr}^{+6} \text{ (UVA emerald green)} \]

Diagram:
- **UV** region
- **Visible region**
- **IR** region

Graph:
- **% Transmittance**
- **Wavelength, nm**

Lines:
- **UVA Emerald green**
- **Emerald green**
Cobalt Oxide

- Only one oxidation level of cobalt oxide gives color to glass.
- $\text{Co}^{+2}$ has an absorption at 530, 590 and 650 nm.

Blue
Cupper Oxide

- Cupper oxide exists in two oxidation states in glass.
- The color caused by cupper oxide depends on the oxidation level of cupper.
- $\text{Cu}^{+1}$, has no absorption in visible region.
- $\text{Cu}^{+2}$, has an absorption at 780 nm.

Turquoise blue
Manganese Oxide

- Manganese oxide exists in two oxidation states in glass.
- The color caused by manganese oxide depends on the oxidation level of manganese.
  - Mn$^{+2}$, has no absorption in visible region.
  - Mn$^{+3}$, has an absorption at 470-520 nm.
Selenium

- Selenium has four oxidation states.
- But two of them are rarely exist (Se$^{4+}$, Se$^{6+}$) in glass.
- Se$^{0}$ and Se$^{-2}$, has an absorption at 490 nm.
Decolorizing

In every type of glass, $\text{Fe}_2\text{O}_3$ comes from the natural raw materials as an impurity. In colorless glasses, decolorization is necessary in order to eliminate the greenish color of iron oxide.
Thermal Analysis of Glasses

1 INTRODUCTION

Thermal analysis methods are used for determination of a number of important properties of glasses. The glass transformation and fictive temperatures of glasses, discussed in Chapter 7, are commonly measured using a *differential scanning calorimeter* (DSC). Crystallization kinetics can be measured by a number of different methods, but the fastest and most commonly used methods rely on various techniques using the DSC. The determination of nucleation rate versus temperature curves can also be carried out using a DSC. Access to a DSC has become a requirement for any glass science laboratory.

2 DIFFERENTIAL SCANNING CALORIMETERS

The differential scanning calorimeter evolved from an older instrument known as a differential thermal analyzer, or DTA. The DTA, which is based on the work of Le Chatelier in 1887, was developed in 1899 for identification of specific types of clays, which are difficult to differentiate by more traditional methods. The concept of the DTA is quite simple. A differential thermocouple, which consists of two otherwise identical thermocouples connected in opposing polarities, is placed in a furnace in a position which allows the bead of one thermocouple to be inserted into an inert reference material, while the bead of the other thermocouple is inserted into the sample. The difference in temperature between the reference and sample materials is obtained directly as a function of temperature as the entire assembly is heated at a controlled, usually linear, rate. In the absence of any thermal difference between the sample and reference material, the output of the differential thermocouple will be zero. When a thermal event occurs, e.g., heat released during crystallization, the change in specific heat at the glass
transformation, absorption of heat during phase transformations, or the heat of reaction of a wide variety of chemical processes, the temperatures of the sample and reference will differ, indicating that some change is occurring in the sample, (the reference is assumed to be totally inert and free of any thermal events). Once the temperature rises beyond the region of change in enthalpy, the difference between the sample and reference will return to zero, yielding a curve of $\Delta T$ versus temperature which has peaks at exothermic or endothermic events, or an offset in the baseline due to a change in heat capacity of the sample.

The DTA is very useful for determination of melting points of crystals and glass transformation and crystallization temperatures of glasses. The design of a DTA, however, makes it difficult to deter-
A typical DSC curve for a glass where crystals form during heating and then melt at a higher temperature is shown in Figure 12.1. The first

![DSC curve](image)

**Figure 12.1** DSC curve exhibiting a change in specific heat at the glass transformation, an exothermic peak due to crystallization of the glass, and an endotherm due to melting of the crystals formed at the exotherm.
temperature. The thermal event indicative of $T_g$ is the discontinuous change in the specific heat of the material, which occurs as the glass converts from a solid to a liquid in the glass transformation region. The increase in specific heat will cause an increase in the thermal lag of the sample relative to the inert reference material, resulting in a shift in the baseline, or offset, of the curve. The magnitude of the specific heat can be determined from this shift, as is discussed later in this chapter.

The next feature in this curve encountered during heating is an exothermic peak due to crystallization of the glass as the enthalpy of fusion is released from the sample. Crystallization of glasses may range from the example shown here, where a single phase is formed, to very complex curves, with multiple peaks, which may or may not overlap, resulting from the formation of a number of crystalline phases (see Figure 2.4).

The endothermic peak at the highest temperature is due to melting of the crystals formed during heating. Endothermic peaks may also occur due to the presence of crystals which formed in the sample during cooling of the melt, or during some prior thermal treatment outside the DSC. Endothermic peaks may also occur due to the solid–solid transformation of a crystalline phase already existing in the sample, or of a phase formed by crystallization earlier in the heating process, e.g., a peak resulting from the endothermic $\alpha\rightarrow\beta$ transformation of quartz, which is often found in curves for glass-ceramics.
3 GLASS TRANSFORMATION TEMPERATURES

Determination of $T_g$ using a DSC is based on a similar concept, with the replacement of the change in volume by the change in specific heat which also occurs at $T_g$. The specific heat of the material will change rather abruptly as the solid converts to the liquid. The onset of the change in specific heat is commonly used as an indicator of the temperature range of transition, just as the onset of the change

![Graph showing the output signal (volts) vs temperature (°C) with a peak indicating $T_g$.]

Figure 12.2 An example of the determination of $T_g$ from a DSC curve
Glass Technology

1 INTRODUCTION

Manufacturing of commercial glass products involves application of all of the principles discussed earlier in this book. Commercial production, however, requires expansion of these principles to very large scale melting, and to the unique forming methods required for each type of product. Production of tubing from vitreous silica requires a completely different approach than production of bottles or window glass. Processing of traditional bulk consumer products differs greatly from the more sophisticated processing required for optical fibers and glass-ceramics. Non-melting methods of forming glasses, including vapor deposition and sol-gel processing, also deserve a brief discussion. Detailed discussions of glass technology can be found in several books dealing exclusively with that subject.

2 CLASSICAL FORMING METHODS

2.1 Containers

Glass containers were originally hand blown. A gob of glass was gathered on the end of a blowpipe by dipping the pipe into a melt. Air was forced into the gob by blowing through the pipe, forming a hollow shell of glass around a bubble at the end of the pipe. The object was continually rotated and shaped by hand using paddles formed from wood which had been charred and soaked in water. Containers formed by this method were expensive and highly variable in quality.
Most common containers are made from soda–lime–silica glasses containing, in wt%, roughly 73% silica, 11% lime, 14% soda, and 2% alumina. These glasses also may contain very small quantities of MgO, K₂O, and SO₃, which is used as a fining agent. Specialized containers for chemicals and pharmaceuticals may be made from borosilicate glasses, which have an increased durability and do not release sodium into the contents through chemical attack on the glass.

2.2 Flat Glass

Flat glass was originally formed by hand by gathering a gob on the end of a pipe and then spinning the gob inside the furnace until it flattened due to centrifugal force (the crown method). Glass panes were cut from the outer portions of the disk. These panes were thinner at the outer edge of the disk and thicker toward the center of the disk. Installation of these panes with the thicker edge down has been proposed as an explanation for the observation that some windows in ancient cathedrals are thicker at the bottom edge. (The false attribution of this observation to flow of the glass remains one of the great myths of science). The center of the disk, called the bullseye, was used as a crude lens or in decorative leaded glass windows.

Larger sheets of glass could be produced by blowing the gob into a cylindrical shape (broad glass), or by drawing a very large cylinder (machine cylinder method), from the melt. These cylinders were split parallel to their axis and flattened by reheating on a flat surface. The quality of the glass was poor, but larger sheets could be produced than by the crown method.

Continuous formation of flat sheets (sheet glass) can be performed by drawing a ribbon directly from the melt. Different commercial techniques involve variations in the method used to control the initial point of ribbon formation, and in the direction of draw. All commercial processes for making sheet glass include...

Most modern glass sheet is produced using the float process (*float glass*), in which the melt flows from the glass tank directly onto the surface of a bath of molten tin. The upper surface of the melt is in contact with the atmosphere above the tin bath, which must be reducing to prevent oxidation of the tin. Since neither surface contains any flaws,

### 2.3 Glass Fibers

Glass fibers, or *fiberglass*, are widely used for thermal insulation, fire resistant textiles, and reinforcing fibers for composites. Chopped, or discontinuous fibers, can be produced by several techniques in which a thin stream of highly fluid melt flowing from the bottom of a container is broken into small segments by air jets, mechanical attenuation, or flame attenuation. While these methods are still occasionally used, the most commonly used method for production of discontinuous fiber, *rotary processing*, is similar to the process used to make "cotton candy" from molten sugar. The glass stream falls into a spinning cylinder which has a large number of holes in its surface. Centrifugal forces extrude the melt through these holes into a high-velocity gas stream, which breaks the fibers into small lengths.

Continuous fibers are produced either directly from the original melt or from remelted glass marbles. The latter method allows production of
A number of compositions are used to produce fiberglass. Insulation fibers are produced from modified soda–lime–silica compositions, which contain more alumina and iron than container glasses. Most of the continuous fiberglass is produced from so-called \textit{E} glass, which actually includes a range of alkaline earth aluminoborosilicate compositions. This family of compositions was originally developed for applications requiring high electrical resistivity. If \textit{E} glass fibers are exposed to strong mineral acids, they are leached until only a silica framework remains. If the leached glasses are consolidated by heat treatment, high-silica fibers are formed. Other common fiberglass products are made from \textit{S} (for strong) \textit{glass} and \textit{C} (for corrosion-resistant) \textit{glass}. \textit{S} glass contains more alumina than \textit{E} glass, while \textit{C} glass contains more silica and less alumina than \textit{E} glass.
Glass-Ceramics

Glass-ceramics are fine-grained polycrystalline materials formed when glasses of suitable compositions are heat treated and thus undergo controlled crystallization to the lower energy, crystalline state. It is important to emphasize a number of points in this statement on glass-ceramics. Firstly, only specific glass compositions are suitable precursors for glass-ceramics; some glasses are too stable and difficult to crystallize, such as ordinary window glass, whereas others crystallize too readily in an uncontrollable manner resulting in undesirable microstructures. Secondly, the heat treatment is critical to the attainment of an acceptable and reproducible product.

Usually a glass-ceramic is not fully crystalline; typically the microstructure is 50vol% to 95vol% crystalline with the remainder being residual glass.
The mechanical properties of glass-ceramics are superior to those of the parent glass. In addition, glass-ceramics may exhibit other distinct properties which are beneficial for particular applications, as exemplified by the extremely small coefficient of thermal expansion of certain compositions in the Li$_2$O-Al$_2$O$_3$-SiO$_2$ system which consequently are suitable for thermal shock resistant applications.

**The Glass Crystallization Process**

The crystallization, or devitrification, of glass to form a glass-ceramic is a **heterogeneous transformation** and as such consists of two stages, namely a nucleation stage and a growth stage. In the nucleation stage small, stable volumes of the product (crystalline) phase are formed, usually at preferred sites in the parent glass. The preferred sites are **interfaces** within the parent glass or the **free surface**. The latter (growth) is usually undesirable as the resulting glass-ceramic microstructure often consists of large oriented crystals that are detrimental to mechanical properties.
Once a stable nucleus has been formed the crystal growth stage starts. Growth involves the movement of atoms/molecules from the glass, across the glass-crystal interface, and into the crystal. The driving force for this process is the difference in volume or chemical free energy, $\Delta G_v$, between the glass and crystalline states. The transport of atom/molecules across the interface is thermally activated with an associated activation energy $\Delta G_a$. 
1) Conventional Method (Two-Stage)

The conventional method for producing a glass-ceramic is to devitrify a glass by a two-stage heat treatment (Figure 1 (b)). The first stage is a low temperature heat treatment at a temperature that gives a high nucleation rate (around $T_N$ in Figure 1a) thus forming a high density of nuclei throughout the interior of the glass. A high density of nuclei is important as it leads to a desirable microstructure consisting of a large number of small crystals. The second stage is a higher temperature heat treatment at around temperature $T_G$ to produce growth of the nuclei at a reasonable rate.

Figure 1
2) Modified Conventional Method (Single-Stage)

The reason for the two-stage heat treatment of the glass is a consequence of the limited overlap between the nucleation and growth rate curves (Figure 1 (a)). If there is extensive overlap of the rate curves then nucleation and growth can take place during a single-stage heat treatment at temperature $T_{NG}$ as indicated in Figure 2. The rate curves, particularly the nucleation rate curve, is sensitive to composition and hence by optimizing the glass composition it is, in some cases, possible to obtain the necessary overlap.

![Diagram showing rate of nucleation and growth](image)
3) Powder Methods
The shaping by cold-compacting a powder followed by a high temperature heat treatment to sinter the compact is a common route for the fabrication of ceramics and it has been also employed for glass-ceramic production.

4) Sol-Gel Precursor Glass
So far only glasses produced from the molten state have been considered but in the last decades there has been considerable interest in using sol-gel and colloidal techniques to obtain the precursor glass in either powder or bulk form.
Glasses crystallization

- Crystallization in glasses is generally a phenomenon to be avoided if at all possible. Crystallization makes glass opaque, for example, and does improve its other properties.
- The exception is the case of glass-ceramics.
- Most glass-ceramics are valued for a combination of chemical inertness and thermal shock resistance.
- Thermal shock resistance depends on low CTE. Low CTE means that strains developed on cooling from high temperatures generate small stresses and the breaking strength is less likely to be exceeded.
Glass Ceramics

- Other glass ceramic materials are optimized for:
  - High mechanical strength
  - High temperature capability
  - Photosensitivity
  - Low dielectric constant (electronic packaging)
  - Dielectric-breakdown resistance
  - Biological compatibility
  - Machinability (through the inclusion of micaceous phases)
Applications of Glass Ceramics

- Radomes - Corning 9606, cordierite glass-ceramic. Required properties: transparency to radar, low dielectric constant, low CTE, high strength, high abrasion resistance, high thermal shock resistance.

- Photosensitive glass-ceramics based on lithium disilicate, Li$_2$Si$_2$O$_5$, as the crystalline phase that can be selectively etched (UV light) to develop very fine features (holes, channels etc.). The parent glass has lithium metasilicate. Example: Foturan, Fotoceram.

- Machinable glass-ceramics, e.g. MACOR, based on fluorine-phlogopite, KMg$_3$AlSi$_3$O$_{10}$F$_2$), with additions of B$_2$O$_3$ and SiO$_2$ to form a glass. The fluorine compound is micaceous which allows easy cleavage over short distances. The material is very useful as a machinable insulator, used in welding equipment, medical equipment.
Applications, contd.

- Substrates for magnetic recording disks. Spinel-enstatite glass-ceramics allow high modulus, high softening point (≈1000°C), high toughness, insulating substrates.

- Cookware based on glass-ceramics with beta-spodumene, LiAlSi$_2$O$_6$-SiO$_2$, e.g. Corning Ware 9608. The latter compound has low CTE, is white in color, and can be easily fabricated.

- Low expansion glasses such as Zerodur containing mainly beta-quartz. These are useful for telescope mirrors and ring lasers (low He permeability also essential here).
Zerodur (notation of the manufacturer: ZERODUR®), a registered trademark of Schott AG, is lithium-aluminosilicate glass-ceramic. It has been used for a number of very large telescope mirrors. With its very low CTE it can be used to produce mirrors that retain acceptable figures in extremely cold environments such as deep space. Its thermal expansion coefficient is in the range of $\sim 10^{-9}$.
Microstructure development

- The history of glass-ceramics starts with a mistake by a researcher (Stookey) who left an oven on at too high a temperature with a sample of lithium silicate glass containing silver. He expected to find a puddle of glass once he realized his mistake, but instead found a piece of white ceramic because his glass had crystallized with a fine grain size.

- This lead to the use of titania as a nucleating agent in alumino-silicate glasses.

- Control of crystallization (=devitrification) depends on inclusion of a (well dispersed) nucleating agent. This is akin to grain refinement in solidification (addition of TiB$_2$ to aluminum melts).
Nucleation + Growth

• In contrast to metals, where isothermal treatments are common, two-steps anneals in glass-ceramics are the norm.

• The typical sequence involves a nucleation step of a small volume fraction of, e.g. TiO₂, followed by bulk growth of other phases.

• The nucleation step is carried out at lower temperatures, presumably to obtain higher driving forces.

• The growth step is carried out at higher temperatures, again presumably to obtain higher growth rates (more rapid diffusion).
Heat Treatment of Glass-Ceramics

- Typical heat treatments require cooling past the "nose" of the crystallization curve, followed by a low temperature treatment to maximize nucleus density and finally a higher temperature treatment to grow the grains.

[Chiang]

**Fig. 5.75** Typical processing cycle for Li$_2$O-Al$_2$O$_3$-SiO$_2$ glass ceramics.
Nucleation, grain size,

Fig. 5.76 (a) Microstructure in Li$_2$O-Al$_2$O$_3$-SiO$_2$ glass ceramic held at 775°C for 2 h. before heating to 975°C for 2 min.

Low temperature nucleation step included -> fine grain size

Fig. 5.76 (b) Identical composition heated rapidly to 875°C and held for 25 min. (From P.E. Doherty in R.M. Fulrath and J.A. Pask, Eds., Ceramic Microstructures, John Wiley and Sons, New York, 1988, pp. 161-185.)

Rapid heating to high temperature (875°C)
Nucleation Rate - Viscosity

- There is a useful relationship between viscosity and nucleation rate for crystallization in glasses.
- The nucleation rate, $N$ (or $l_N$), is determined by the critical free energy for nucleation and a Boltzmann factor as seen previously:

$$
\Delta G^* = \frac{16\pi\gamma^3}{3\Delta G}\sqrt{\Delta G}
$$

$$
N = \omega C_0 \exp\{-\frac{\Delta G^*}{kT}\}
$$

where $\omega$ is an attempt frequency or vibration frequency of order $10^{11}$ per second, $C_0$ (or $N_N$) is the density of molecules per unit volume of order $10^{29}$ per m$^3$.

- In glasses one must adjust the attachment frequency based on the viscosity since this can vary so markedly with temperature. Using the Stokes-Einstein relation for atomic diffusivity in a melt:

$$
D = \frac{kT}{3\pi a_0 \eta} = \omega a_0^2
$$

- This suggests that we can take $\omega$ to be inversely proportional to the viscosity, $\eta$. 
Viscosity dependent nucleation rate

- Adjusting the attachment frequency to match experimental data (larger than theory suggests),

\[ N = 40 \frac{C_0 kT}{3\pi a_0^2 \eta} \cdot \exp\left(-\frac{\Delta G^*}{kT}\right) \]

- Given that the viscosity dominates the temperature dependence of all the terms in this expression, we can simplify to this:

\[ N = \frac{K}{\eta} \cdot \exp\left(-\frac{\Delta G^*}{kT}\right) \]

*where* \( K \) *is a constant of order* \( 10^{36} \text{ m}^{-3}\text{sec}^{-1}\text{poise} \) *for oxide glass formers.*
Viscosity dependent nucleation rate

- In the previous development of driving forces, we approximated the driving force as $\Delta T \frac{L_f}{T_m}$, where $L_f$ is the latent heat of transformation (melting, e.g.). Hoffmann developed the following improved approximation for the case that the difference in specific heat between solid and liquid is significant but constant (with changing temperature):

$$\Delta G_m = \Delta H_m \Delta T \frac{T}{T_m^2}$$

- This can be inserted into the standard expression for nucleation rate:

$$N = \frac{K}{\eta} \exp\left\{\frac{16\pi}{3kT} \frac{V_m^2 \gamma_{SL}^3}{\Delta H_m^2 \left(\frac{\Delta T \cdot T}{T_m^2}\right)^2}\right\}$$
Heterogeneous nucleation

- Heterogeneous nucleation is as important in glasses as it is in metals.
- In glass, one must be careful to avoid including phases that can act as nucleation sites for crystallization.
- In glass-ceramics, the situation is reversed and one typically adds nucleating agents deliberately.
- Examples are TiO$_2$ and ZrO$_2$. 
Typical glass ceramic compositions

- Low expansion glass ceramics result from the particular compositions used.
- Al and Li substitute into beta-quartz (silica): $\text{Al}^{3+}$ substitutes for $\text{Si}^{4+}$ with Li$^+$ providing charge neutrality as an interstitial ion.
- Lithia-alumina-silica compositions for Pyroceram contain beta-spodumene, $\text{LiAl}[\text{Si}_2\text{O}_6]$, which has a weak positive CTE, $\sim 10^{-6} \cdot ^\circ\text{C}^{-1}$.
- At higher levels of Al and Li substitution, the CTE can become negative.
- Substitution limit is beta-eucryptite, $\text{LiAl}[\text{SiO}_4]$. 
Design of Medical Glass-Ceramics

7.1 Glass Ceramic Fabrication

The art of glass-ceramics was first established with the publication of US Pat. No. 2,920,971. Classically, a glass-ceramic is made through controlled heat treatment of a precursor glass. The manufacture of a glass-ceramic involves three general steps:

- Preparation of a glass-forming batch from raw materials, oxides, and nucleating agents.
- The batch is melted and then cooled to a temperature within the transition range to yield a glass.
- The glass is then heated to a temperature above the transition range to perform glass crystallization.

A homogeneous glass batch is prepared using high-quality raw materials that are fused in a high temperature resistant crucible to form a homogeneous molten glass. The melt is then cooled into a glass body with the desired shape. The glass is then annealed at a temperature close to the transition temperature.

The crystallization process, the development of crystalline phases in the glass matrix, comprises two main steps. In the first step, the glass is heated to a temperature slightly above the transformation range and maintained for a sufficient time to achieve substantial nucleation. In the second step, the nucleated body is heated to a higher temperature, frequently above the softening point of the precursor glass to allow the growth of crystals on these nuclei. A homogeneously crystallized glass ceramic with relatively uniform size can be prepared with careful heat treatment.

The glass-ceramic is generally highly crystalline and the crystals themselves are very finely grained and preferably dispersed uniformly in the glass matrix. A wide
While the art of dental porcelain is similar to the technique of glass ceramics preparation, the porcelain term here refers to a glass ceramic made by sintering of amorphous glass frit powders under controlled crystallization, but it is of course glass ceramic made by crystallization of powder glass. The starting materials for the glass ceramics are amorphous glasses that successfully crystallize in a controlled process.

The glass ceramic can be produced by three different processes, namely:

- The process of obtaining glass by fusing a mixture of raw materials and then solidifying into glass blocks which are reheated to develop nuclei and then treated at higher temperature to develop crystal phases in the glass.
- The process of obtaining glass by fusing a mixture of raw materials, solidifying by quenching into glass frits and milling the frits into fine powders which are then pressed, and heat treated to achieve full sintering and develop crystal phases in the glass matrix.
- The process of obtaining amorphous glass powder by subjecting a gel based on metal alkoxide compounds, to a high-temperature heat treatment. The powder is then ground, shaped, and heat-treated to form crystals in the amorphous glass matrix.

Because glass-ceramics have a crystallinity content generally greater than 50 vol.%, they are normally mechanically stronger than their parent glasses. Hence, annealed glass bodies conventionally demonstrate a modulus of rupture (MOR) value in the range of about 35–60 MPa, whereas glass-ceramic products created from these glasses will exhibit moduli of rupture in the range of 70–300 MPa.

In general, the crystallization process is time–temperature related. Therefore, only short exposure periods will be required at the higher temperatures, e.g., half an hour or even less; whereas much longer periods of time will be employed at lower temperatures, e.g., up to 24 h or more.
7.3 Selection of Glass Compositions for Glass Ceramics Processing

There are several criteria that should be considered in the selection of glass compositions for glass ceramic processing. The glass must be capable of being crystallized without the use of a long schedule of heat treatments. The constituents of the glass and their proportions must be chosen to encourage the development of a certain crystalline phase and produce the desired characteristics. For example, the potassium aluminosilicate glasses, especially the stoichiometric leucite compositions are very difficult to crystallize. Thus, glasses of such compositions are of very high stability, poor crystallinity, and insufficient crystal growth and should be avoided or modified when seeking to fabricate glass ceramics.

On the other hand, in glasses that contain a fairly high proportion of modifying oxides, these oxides weaken the glass network structure by introducing non-bridging oxygens, which link to the adjacent silica tetrahedra. As the proportion of non-bridging oxygens increase, the network structure becomes increasingly destabilized. However, the atomic rearrangement, which is so necessary for the proposed crystallization, is made possible. Li₂O, Na₂O, and K₂O are useful modifying constituents during the glass ceramic crystallization process. Alternatively, the alkaline earth oxides, such as ZnO, MgO, and CaO, are useful for enhancing the crystallization process.

A range of glass compositions, shown in Table 7.1, can be used to develop mica–cordierite glass ceramics by heat treatment at temperature between 650 and 1,020°C.

<table>
<thead>
<tr>
<th>Oxides</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>MgO</th>
<th>Na₂O</th>
<th>K₂O</th>
<th>F⁻</th>
<th>CaO</th>
<th>P₂O₅</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>45.2</td>
<td>29.6</td>
<td>12.0</td>
<td>3.9</td>
<td>4.5</td>
<td>4.2</td>
<td>0.1</td>
<td>0.3</td>
</tr>
<tr>
<td>2</td>
<td>47.3</td>
<td>25.7</td>
<td>11.1</td>
<td>3.1</td>
<td>4.8</td>
<td>3.5</td>
<td>0.5</td>
<td>4.0</td>
</tr>
<tr>
<td>3</td>
<td>43.6</td>
<td>26.3</td>
<td>14.7</td>
<td>5.2</td>
<td>4.3</td>
<td>4.5</td>
<td>0.1</td>
<td>1.1</td>
</tr>
</tbody>
</table>
7.4 Optimum Heat Treatment Conditions

The crystallization of glass into glass ceramics is normally guided by the thermal analysis data. The heat treatment converts the glass objects into uniform microcrystalline glass ceramics with superior properties compared with the parent glass. In addition, the development of a finely divided uniform microstructure or interlocking microstructure results in improvements in the strength and encourages the development of a range of desirable glass ceramic properties. The factors that control crystallization are the heating rate, nucleation temperature, crystallization temperature, and the length of heating time.

Efficient nucleation leads to the production of large numbers of small crystals rather than small numbers of large crystals, which is the main target of the glass ceramic process. Then, it is necessary to elevate the temperature of the nucleated glass in order to permit crystal growth upon the developed nuclei. This must be done at a carefully controlled rate of heating in order to avoid the deformation of the glass ceramic during the crystallization process. If the rate of heating is too high, the rate of crystal growth may not be sufficiently rapid and this could result in glass deformation. In contrast, if the rate of heating is low, deformation is less likely to happen as the remaining glassy phase decreases progressively with temperature elevation.
7.5 Prediction of the Proper Glass Heat Treatment Schedule

The prediction of the proper heat treatment schedule is executed using various techniques depending on the type and nature of materials. In the current case, the proper heat treatment for the starting glass include many steps depending on many factors. The first factor is to know the mechanism of crystallization, i.e., whether it is bulk volume crystallization or surface crystallization. Then according to the type of crystallization mechanism, the heat treatment steps can be scheduled. The glass is used in the form of a powder in the case of surface crystallization or bulk glass in the case of volume crystallization.

![Graph showing the transition and softening temperatures of a glass](image)

Fig. 7.4 The measurement of the transition ($T_g$) and softening ($T_s$) temperatures of a glass based on the thermal expansion curve
7.5.1.1 Annealing Temperature Determination

Annealing is very important as it removes as much as possible the stresses developed in the glasses during the heating or casting. It is known that non-annealed or badly annealed glasses are difficult to handle, cut or polish and in addition they can spontaneously shatter during handling due to the developed stresses, which can be very dangerous. Thus, it is important to determine the right annealing temperature of a glass before handling the glass or processing it into a glass ceramic, particularly in the case of glasses that crystallize by a volume crystallization mechanism.

The annealing temperature can be determined from either the expansion curve as shown in Fig. 7.4 or from the DTA curve as shown in Fig. 7.5. By knowing the transition temperature ($T_g$), it is possible to know the right annealing temperature, which lies within the annealing range between the upper and lower annealing temperatures. The transition temperature is the temperature at which a glass melt change

![Diagram showing $T_g$ and $T_s$ temperatures of a glass based on the DTA curve.](image)

into an amorphous solid and generally is estimated to be close to the annealing point of the glass. In most cases, the correct annealing step is to choose a temperature close to the transition temperature, typically within 25–50°C.
7.5.1.2 The Nucleation Temperature

The nucleation temperature of glasses is best determined from a DTA curve. The preferred nucleation is to heat the glass to a temperature above the transition temperature \( T_g \) for a sufficient time to assure good nucleation. In some cases, the nucleation temperature may be higher or lower in glasses with a wide transition range of temperature depending on the parent glass composition. In other words, the optimum nucleation temperature occurs between the transition temperature \( T_g \) and a temperature some 50–100°C above \( T_g \). In addition, the nucleation temperature is determined to be close to the lowest temperature in the endothermic reaction corresponding to \( T_s \) as shown in the DTA curve in Fig. 7.5.

7.5.1.3 The Crystallization Temperature

When the nucleated glass is exposed to a secondary heat treatment at temperatures higher than the glass transition temperature \( T_g \), the crystallization process starts. The crystallization temperatures can be determined from the DTA curve to be at the temperature corresponding to the exothermic peak or peaks as shown in the example in Fig. 7.5. One or more phases can crystallize from the glass through exothermic reactions. The nucleated body should be heated to or slightly higher than the crystallization temperature for a time sufficient to induce crystal growth without the dissociation of the predominant crystal phase. In other words, the crystallization range lies above the nucleation temperature and a temperature slightly lower than the temperature at which the predominant crystalline phase starts to redissolve.
7.6 Interpretation of a Differential Thermal Analysis Curve

The chemical reactions or structural changes within crystalline or amorphous substances are accompanied by the evolution or absorption of energy in the form of heat. For example when a glass substance crystallizes, an exothermic reaction occurs since the free energy of the developed regular crystal phase is less than that of the structurally disordered glass substance. The melting of a crystalline glass ceramics is represented by an endothermic reaction as the liquid state needs higher free energy than that of the glass.
Also chemical reactions between two materials can give rise to either endothermic or exothermic reactions. From the shape of the melting endothermic peak, it can be predicted if the glass ceramic is monocristalline phase or multiphase. In general, the endothermic peak relating to the melting of the monophase glass ceramic is always sharp with steep dip as shown in Fig. 7.6. Thus, differential thermal analysis (DTA) is a technique that facilitates the study of phase development, decomposition, or phase transformations during the glass ceramic process with heating.

In this method the glassy materials under test is in the form of finely divided powders placed in a small crucible of platinum or other suitable refractory crucible such as aluminum oxide. Adjacent to the test crucible is a second crucible containing an inert powder such as aluminum oxide, which does not exhibit endothermic or exothermic reactions. The temperature differences between the tested sample and the reference sample powder (inert alumina) are recorded during heating and the differential temperature is plotted. The exothermic reactions are represented as peaks and the endothermic reactions are represented by dips on the DTA curve.

The technique is considered a useful method for the investigation of the glasses and the determination of the optimum temperatures at which the different crystal phases are formed. The quality and the shape of the peaks are affected by the rate of heating and the fineness of the powder.

As the temperature is increased, a dip is observed on the DTA curve due to slight absorption of heat that occurs when the annealing point of the glass is reached. With further increase of the temperature, one or more quite sharp exothermic peaks can be expected, corresponding to the appearance of various crystalline phases. At higher temperature, an endothermic reaction peak relates to the early incongruent melting of the predominant crystalline phase. Figure 7.7 shows the main features that can be determined from the typical DTA curve of a glass.
Fig. 7.7 DTA of fluorrichterite–enstatite glass ceramics

Thus, the DTA analysis yields a great deal of very useful information, which is of great help in designing the heat treatment schedules for the crystallization of a glass into a glass ceramic. The curve not only indicates the temperature range in which the nucleation and crystallization occurs, but it also indicates the maximum temperature to which the glass ceramics can be heated without exposing the glass ceramic to deformation due to melting of the crystal phases.
7.8 Significant Points on the Thermal Expansion Curve

Several significant points in the expansion curve can be predicted from the thermal expansion curve of a glass, including the lower annealing point, transition temperature, the upper annealing point, and the softening point in addition to the nature of the melting (Fig. 7.10).

Fig. 7.10 Significant points along the thermal expansion curve of a glass, where $T_1$ is the lower annealing or strain release temperature, $T_g$ is the transition temperature, $T_u$ is the upper annealing temperature, and $T_s$ is the softening temperature.