CHAPTER 2 THEORY

A glass is defined as "an inorganic product of fusion which has been cooled to a rigid condition without crystallization". There are some differences between glass and crystals. The main distinction between glass and crystals is the presence of long range order in the crystal structure. Glass materials are polycrystalline solids containing nanometer to micrometer size crystals embedded in a residual glass matrix. Glass is amorphous solids. Glass applications can be determined from physical, optical, luminescence and scintillation properties, etc, depending on user's objectives. An important method in modifying and tuning glass properties depend on user's objectives is rare-earth doped in glasses.

2.1 Definitions of Glass [32]

Humans have been producing glasses by the melting of raw materials for thousands of years. Egyptian glasses date from at least 7,000 B.C. The origin of the word glass is the Latin term "glaesum", which refers to a lustrous and transparent or translucent body. Glassy substances are also called *vitreous*, originating from the word *vitrum,* again denoting a clear and transparent body. Although glasses became a popular commodity in the growth of civilization, because of its transparency, luster (or shine) and durability, the understanding of glass no longer requires any of these characteristics to distinguish it currently from other substances. Glasses can be inorganic (non-carbon-based) as well as organic (carbon-based), and fusion is not the only method to make glasses. Glasses are traditionally formed by cooling from a melt. Most of traditional glasses are inorganic and non-metallic. A glass can be defined as "an amorphous solid completely lacking in long range, periodic atomic structure, and exhibiting a region of glass transformation behavior." Any material, inorganic, organic, or metallic, formed by any technique, which exhibits glass transformation behavior is a glass. The American Society for Testing and Materials (ASTM) definition that glass is an inorganic product of fusion which has been cooled to a rigid condition without crystallizing is not appropriate.

Glass, as one of the important artificial materials and a major vehicle for East–West cultural and technical exchange, has played a great role in the course of human civilization. Its origin and evolution attract the attention of archeologists and glass scientists worldwide. Unlike a crystal, glass may not be represented by a simple chemical formula. There are no restrictions with regard to the relative numbers of chemically different atoms other than the fact that the valences and/or coordination requirements may need to be satisfied. Glass does not have a sharp melting point when heated. The seemingly rigid solid gradually softens and flows at higher temperatures. At ambient temperatures, the viscosity of glass may be sufficiently high that measurable flow does not occur over millennia-certainly not over practical time scales in typical laboratory experiment. It is doubtful that glass windows in building structures of the Middle Ages have flowed to become thicker at the bottom. In the absence of externally applied mechanical, electrical, thermal, magnetic, and gravitational fields, the properties of glass are essentially isotropic like those of a typical liquid.

The most commonly used model for glass structures today are based on the original ideas of Zachariasen, and are grouped under the term *random network theory.*

Nowadays, Zachariasen's ideas were called *Zachariasen's rules* for glass formation. The structural model offered by Zachariasen provides an approach for describing network structures, whether or not they are glasses. In order to explain glass formation, Zachariasen added the requirement that these networks be distorted in some manner such that long range periodicity is destroyed in order for a glass to form. These distortions can be achieved by variations in bond lengths, bond angles, and by rotation of structural units about their axes.

The properties of glass can be modified or changed with the addition of chemical compounds, elements or heat treatment. Combining glass systems (hosts) with chemical compounds or elements thus allows tuning the physical and optical properties in a wide range depending on the composition. The isotropic of physical properties makes glasses resemble liquids. It follows that the atomic arrangements in glass must display the long-range order typical of liquids. In order not to be overly restrictive, let define glass as a solid with liquid like structure, a *non-crystalline solids or simply as an amorphous solids,* with the understanding that the amorphous characteristic here is intended to describe atomic disorder as evidenced by x-ray diffraction (XRD) pattern, it excludes substances such as "amorphous" powder that may simply be "micro-crystals" and display more or less sharp peaks in XRD pattern. To get a clear picture of the fundamental of glass can be considerate the relationship between enthalpy or volume-temperature diagrams (V-T diagrams) of the glass with respect to a liquid and a crystal.

2.2 The Enthalpy-Temperature Diagram [33]

The first theories advanced to explain why some materials form glasses while other do not, were based heavily on the existing knowledge of the behavior of silicate melts and the structure of silicate crystals. These theories tend to assume that some unique feature of certain melts lead to glass formation for those materials, while the lack of these features prevents the formation of glasses from other materials. These theories are often grouped under the heading of *Structure Theories of Glass Formation*.

Consider a small volume or relationship between enthalpy and temperature of material at a high temperature in liquid form on enthalpy or volume versus temperature diagrams (Figure 2.1). On cooling the enthalpy (volume) gradually decreases along the path. Point corresponds to T_m, the melting point of the corresponding crystal, which may be defined as the temperature at which the solid and the liquid have the same vapor pressure or have the same Gibbs free energy. At this temperature, an infinitely small amount of crystals is in thermodynamic equilibrium with the liquid. However, for a perceptible level of crystallization, some finite amount of undercooling of the liquid to a point below T_m is required. Crystallization occurs if, and only if, (i) there are a sufficiently large number of nuclei present in the mass, ad (ii) a large enough crystal growth rates exists. The location of the point below T_m varies depending upon when the thermodynamic driving force created by the undercooling causes a particular group of atoms to transform from the liquid state to the crystal state, and upon the velocity at which the atoms from the liquid can be transported to the crystal-liquid interface. For these reasons, for shown a wide, shaded region with varying probability representing the crystallization path. A volume shrinkage generally accompanies the crystallization. Upon further cooling the crystals so formed shrink along the crystal line.
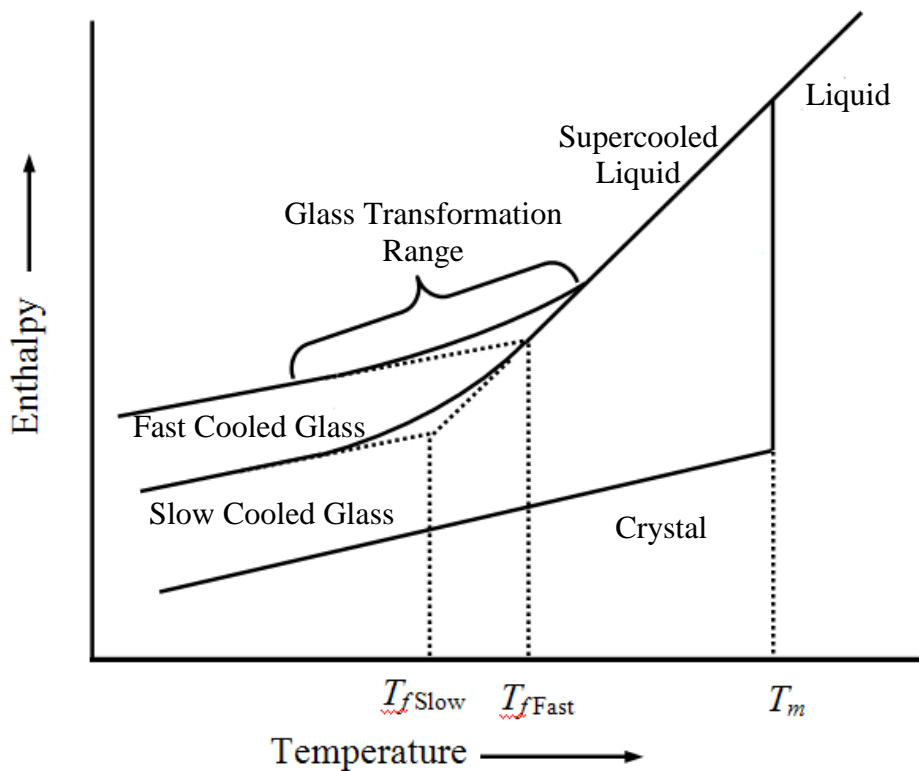
Figure 2.1 Effect of temperature on the enthalpy-temperature of a glass forming melt [33].

If crystallization does not occur below T_m (mostly because the cooling rate is high), the liquid mass moves into the supercooled liquid state along the line, which is an extrapolation. No discontinuities in the Enthalpy-Temperature diagram are observed. The enthalpy (volume), shrinks continuously, i.e., the structure of the liquid rearranges itself into a lower volume along the line required by the lower energy corresponding to the lower temperature. As cooling continues, the molecules become less and less mobile, i.e., the viscosity of the system rapidly increases. At sufficiently low temperatures, the molecular groups cannot rearrange themselves fast enough to reach the volume characteristic of that temperature. The state line then starts a smooth departure and soon become a near-straight line (often roughly parallel to crystal line), ending at point cooled fast or cooled slowly (line below). The material in the near-straight, low-temperature part of the curve behaves essentially as a solid. This is the glassy state.

The smooth curve between the onset of departure from the supercooled liquid line and the completion to a seemingly rigid condition is termed the glass transition region, or the glass transformation range. It must be emphasized that the transition to the glassy state does not occur at a single, sharp value of the temperature. In the upper regions, glass has a viscosity of $\sim 10^8$ Pa.s (10^9 poise) or less, whereas in the glassy state the viscosity of exceeds $\sim 10^{15}$ Pa.s (10^{16} poise) or more to quality for appearance as a solid. The intersection of the extrapolated glass line and the supercooled liquid line is termed the fictive temperature (T_f). One may imagine that T_f is the temperature at which the structure of the supercooled liquid is instantly frozen into the glass

The departure from the supercooled liquid line is the dependent upon the rate of cooling. Slower cooling allows the structure to rearrange itself to stay on straight line somewhat longer, and hence the more slowly cooled glass would be expected to have a lower volume (higher density) and a lower fictive temperature than a more quickly cooled glass (fast cooled glass). For now, it suffices to suggest that the volume of the corresponding crystal is expected to be less than that of the most slowly cooled glass.

When the glass slowly cool is reheated, the state smoothly moves through the transition region along the dashed curve to the supercooled liquid state and ultimately to the liquid state. The Enthalpy-Temperature curve never retraces its path in the transition region. On the other than, the gradually increasing fluidity and, perhaps, a color change due to radiation emission, in general there are no changes in the physical appearance of glass with the reheating.

If the crystals (lower line) are heated, the state will move along crystal line up to the melting temperature (T_m) and melt at T_m and subsequently follow the liquid path. One may question whether it is possible to superheat a crystal or not. Melting produces atomic disorder in a substance and proceeds from the surface inwards. Hence, crystals may be superheated to temperatures beyond T_m if the heat is provided internally or if melting produces a very high-viscosity liquid phase such that atoms within the interior of the crystal do not have "room or time to disorder". Ordinarily, the melting of a crystal is mush sharper (on the temperature scale) than the freezing of liquid.

To understand the structural relationship between the glassy state and other states of matter, we need to understand the pair distribution function and the radial distribution function used commonly to describe the distribution of atoms in amorphous solids.

In multicomponent systems, the temperature T_m is generally identified as the liquidus temperature. At temperatures above the liquidus, the system is completely liquid. Growth of one crystalline phase may occur just below the liquidus. As the temperature is lowered further, more crystalline phases may grow. Measurement of the liquidus temperature is often desirable for large scale glass manufacturing to avoid problems due to devitrification in the glass tank system, or in the finished product, where they appear as inclusions often termed stones. A convenient method is described in ASTM C829-81, where grains of glass are placed in a suitable boat and heated inside a gradient furnace for a desired period of time. Liquidus temperature is located by visually judging the demarcation between clear glass and the appearance of opacity.

A variety of materials form glass readily by cooling from the molten state. It may be recognized that the glass formation range is quite extensive. Many other materials, on the other hand, form a noncrystalline solids only when special techniques or proper experimental conditions, such as cooling from the vapor state, are used. Although glasses can be made by a wide variety of methods, the vast majority are still produced by melting of batch components at an elevated temperature. Regardless of the source of the components used to produce a specific glass, the batch materials can be divided into five categories on the basis of their role in the process: glass former, flux, property modifier, colorant, and fining agent. The main distinction between glass and crystals is the presence of long range order in the crystal structure. Glass materials are polycrystalline solids containing nanometer to micrometer size crystals embedded in a residual glass matrix.
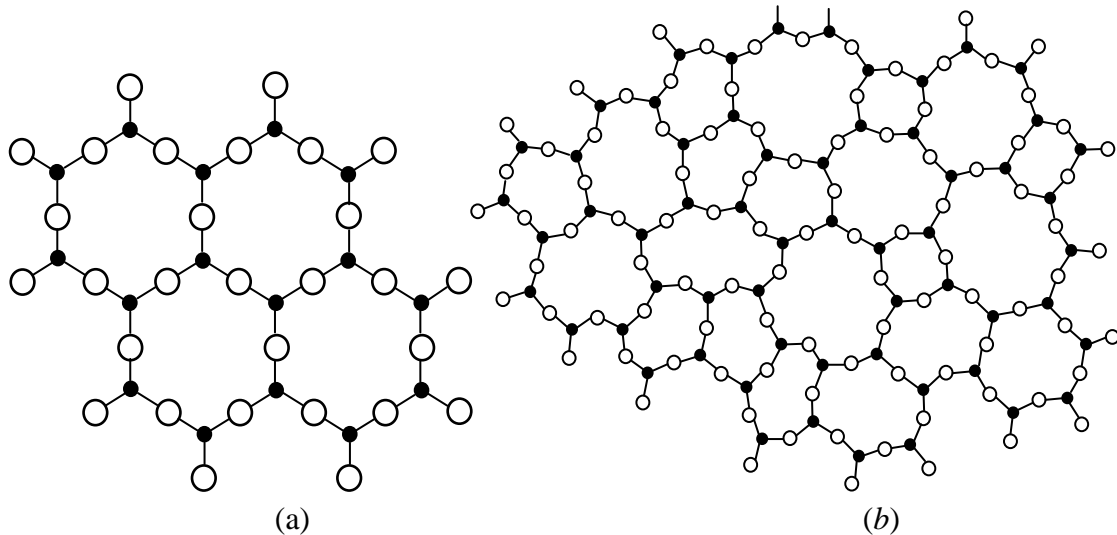
Figure 2.2 A two-dimensional representation of A_2O_3 : (*a*) crystal and (*b*) glass [32].

2.3 Structural Model and Borate Glasses [33, 34]

Amorphous solid or glass, especially borate glasses have been widely investigated and considered for many applications in technological equipment (solid state lasers, optical amplifiers, and electronic equipment). Borate glasses have the highest glass formation tendency, because molten B_2O_3 does not crystallize by itself even when cooled at the slowest rate. It crystallizes only under pressure. Structural models of borate glasses illustrate the function of the modifier content. The cation of a modifier is bonded with oxygen atoms (ionic bonding). Boron occurs in the triangular coordination in vitreous boric oxide. All such triangles are connected by BO at all three corners to form a completely linked network.

Borates glasses with various compositions are interesting due to their linear and nonlinear optical properties. They can be found in high technological applications. The boron atom in borate crystals and glass usually coordinates with either three or four oxygen atoms forming $[BO_3]^{3-}$ or $[BO_4]^{5-}$ structural units. Furthermore, these two fundamental units can be arbitrarily combined to form a super structure, or different B_xO_y. Borate glasses are composed of structural groupings such as boroxol ring, tetraborate, and diborate, etc, that are linked by bridging oxygen. Among these borates, especially the monoclinic bismuth borate BiB_3O_6, shows remarkably large linear and nonlinear optical coefficients. The linear properties (refractive index) of this anionic group should act in a similar way in an amorphous environment. Combining bismuth oxide with boric oxide thus allows tuning of the optical properties in a wide range depending on the composition. Bi_2O_3 does not form glass by itself and bismuth oxide forms glasses with known glass formers as SiO_2, B_2O_3, P_2O_5 and GeO_2.

Consequently, the properties of a glass system Bi_2O_3-B_2O_3 have attracted much interest. A sample of structural borate glass is shown as Figure 2.3, which bonds in a third dimension (van der Waals bonds or force) are very weak and the structure is easily disrupted (low melting point). These well-defined units are connected by oxygen so that the B-O-B angle or B-O-B linkage is variable.
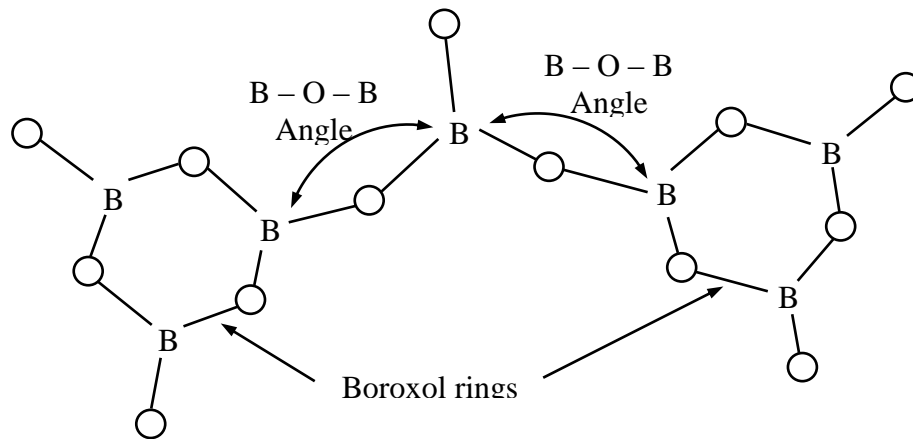
Figure 2.3 Boroxol ring structures in vitreous boric oxide and borate glasses [33].

Adding alkali oxides in borates increases viscosity, and the so-called "boron oxide anomaly" appears. This is a gradual change in the coordination number of boron from 3 to 4 as alkali oxide is added. If the alkali impurity creates non-bridging oxygen, the connectivity of the B_2O_3 network decreases; however, if an alkali impurity causes boron to become tetrahedral coordinated, the connectivity of the network increases. Because the connectivity of a B_2O_3 glass is greatly altered by either of these structural changes, the glass properties are also subject to change. Usually, the property changes resulting from the creation of non-bridging oxygen are directly opposite of the property changes caused by an increase in boron coordination. This interesting structural phenomenon is known as the boron anomaly. Vitreous borates contain a significant fraction of boroxol rings, in contrast to the crystalline B_2O_3. Glassy B_2O_3 contains two boron sites, in a ratio of about 3:1; the more populated site is due to boron in boroxol rings, while the less populated site is due to connecting BO_3 Groups. Vitreous B_2O_3, studied by Raman spectroscopy shows that near the glass-transition temperature the boroxol rings breaks up leading to a more open structure; above the melting point, when the viscosity is low, a regrouping of atoms occurs which results in a low density random network structure. The more open structure of a glass profoundly affects its behavior as a host, allowing greater flexibility so that sites can accommodate metal ions over a much wider range of size and coordination number. Glass transition temperature decreases with increasing network fluidity.
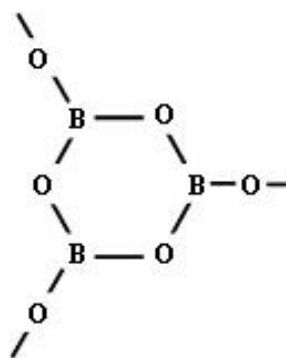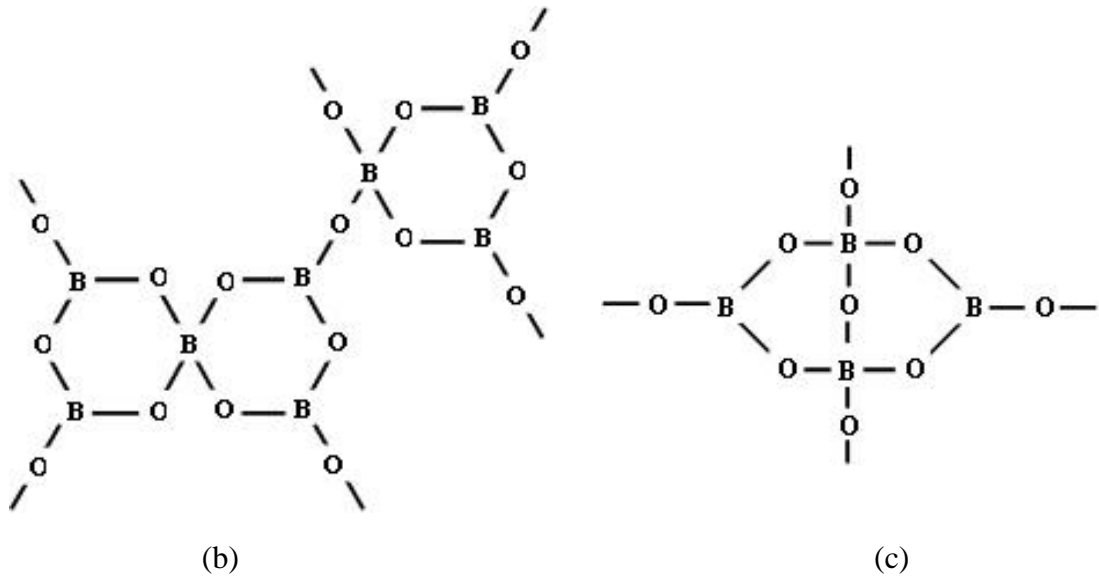

(a)

Figure 2.4 Structural grouping in borate glasses: (a) boroxol ring, (b) tetraborate, and (c) diborate [34].
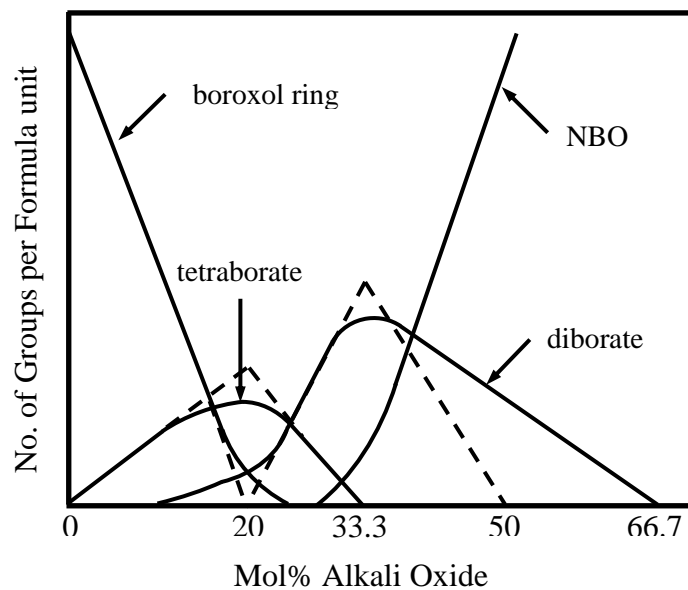

Figure 2.5 Structural model of borate glass as a function of the modifier content (concentrations of intermediate range units in borate glass). Dashed lines correspond to Krogh-Moes' prediction (theory), solid lines represent experimental results [33].

From Figure 2.5, the relative concentrations of these groups are functions of the overall glass composition, which represents a simplified version of the detailed model for these glasses. Although the complete model for these glasses contains a number of other complex intermediate units, Figure 2.5 is adequate to explain the complex behavior summarized under the general term borate anomaly. The maximum in T_g for example, is due to the competing effects of the maximum at about 35 mol% R_2O in the concentration of tetrahedral, which increases the connectivity of the network, and the

formation of NBOs, which begins at $>>$ 25 mol% R_2O, which decreases the connectivity of the network. The relationship between the thermal expansion coefficient and the concentrations of the various units has not been established, but it is interesting to note that the minimum in thermal expansion coefficient occurs just as the boroxol rings disappear, the concentration of tetraborate units passes through a maximum, and where diborate units begin to form. The properties of the borate glasses appear to be strongly connected to the concentrations of the particular intermediate units present in a given glass, while the properties of the alkali silicate glasses are much more simply determined by the relative concentrations of BO and NBOs in the network.

2.4 Density and Molar Volume [33]

The density of a substance is defined as its mass per unit volume, and in the metric system of units is measured in grams per cubic centimeter or kilograms per cubic meter (SI units). The relative density of a solid or liquid is defined as the ratio of the density of the substance to the density of water. Since relative density is a numeric, it has zero dimensions. A convenient method for determining density or specific gravities is one which uses Archimedes' principle. This principle states that when a body displaces a fluid, there is exerted on the body a vertical upward force equal to the weight of fluid displaced. This force is called buoyancy, and it acts at the center of gravity of the displaced fluid.

Since glasses may in general, be regarded as solutions, a more useful property was the molar volume V_M, defined as the volume of one gram mole of glass, and then proceed to define partial molar volumes of the various structural units constitution of the glass. The partial molar volume υ_i of a species i in a solution was defined by

$$\upsilon_i = \left(\frac{\partial V}{\partial n_i} \right)_{n_j, T, P} \tag{2.1}$$

And hence,

$$V_M = n_i \upsilon_i + n_j \upsilon_j \tag{2.2}$$

In essence, the total molar volume is treated as an extensive prosperity in terms of the partial molar volumes of individual species or structural groups. The partial molar volume information can be extracted from the density data of glass where the constituents have been systematically varied. If a A^+ is replaced by B^+ in the glass and occupies the same interstice (without changing its size), it is clear that, although the glass density would increase because of the higher atomic weight of B^+, the partial molar volume of the alkali ion would not change. Any increase in the molar volume would be an increase in the partial molar volume of B^+ relative to A^+. This is likely to have some relation to the relative ionic sizes of the two ions. One may readily note that, although the measurement of density changes in a family of glasses may provide only the trends, the extraction of the partial molar volumes from the density data provides further insight into structure while canceling out the effect of atomic mass.

2.5 Measurement of Density

Density is traditionally measure with using the pycnometer, which allows the measurement of volume of a known mass of the specimen. Commercially available gas pycnometers measure the volume by measuring glass pressure changes in a compartment with and without the specimen. Using Archimedes' principle, one may measure the specimen volume as the buoyancy or buoyant force (the decrease in weight) when the specimen is immersed in 4 ^{0}C water. The buoyancy equals the weight of displaced fluid, which, for water, equals the volume in cm^3. If the glass is attacked by water, then it is advisable to use odorless kerosene as the immersion fluid, and multiply by the density of kerosene to obtain the specimen density. The density of glass is

$$\rho = \frac{w_a}{w_a - w_b} \rho_{fluid} \qquad (2.3)$$

where w_a is the weight of the specimen in air.

w_b is the weight of the specimen in water.

ρ_{fluid} is the density of fluid (kerosene or xylene).

2.6 Optical Properties [33]

There are many advanced and exciting applications of glasses in optics: optical fibers as waveguides for long and fast telecommunications, laser hosts, and optical components for medical and outer space studies. Other modern glass are glasses that change absorption with light level (photochromic) and electric field (electrochromic), glasses for gradient index lenses, the new glasses such as fluorides with different optical properties for silicate planar waveguides, sensors, and chalcogenide glasses with high non-linear optical properties for switching, all optical devices and photonic applications.

For the glass window and the glass bulb to function, the optical transmission property is important. The correction for the failing vision and glass fiber communication are based upon the refractive index, optical dispersion and transmission properties of glass. Beside these, there are many more technological advances where the optical properties of glass play a pivotal role.

The linear refractive index (n), and its dispersive wavelength dependence are important parameters to determine the suitability of oxide glass as optical materials. The propagation of electromagnetic waves depends on the optical constants of materials n and k (the extinction coefficient), where n affects the phase of light waves propagate in the material while k affects its amplitude.

The presence of chemical addition can be altering the refractive index and the transmission range. Glasses are differ considerably in structure and thus in the position and intensity distribution of their electronic absorption and vibrational spectra. Color glass filters are made by adding semiconductors with the band gaps in the visible spectral region during the fusion process.

Visible (VIS) region, light rays are generally referred to by their wavelength λ stated in nanometers or angstroms. Infrared (IR) region, the wave number ($2\pi/\lambda$) with units cm^{-1} is used. Ultraviolet (UV) region, sometimes the energy E (eV units) of the photons is used. For conversion, 1 eV = 1,239.8/λ (nm).

When light travels through a medium, a part of it is reflected from the front surface, a part is absorbed, and the balance is transmitted. The reflectance R at normal incidence for light waves traveling from one dielectric medium to another is given by

$$R = \left(\frac{n_1 - n_2}{n_1 + n_2} \right)^2$$
(2.4)

Where, the refractive index or the index of refraction n is ratio between the speed of light in vacuum and the speed of light in that medium.

When light waves travel from one medium of refractive index n_1 into another medium of refractive index n_2, the incident and the refracted rays remain in the same plane, an incident angle i and refractive angle r (angles between the ray and the normal line) are related through Snell's law or law of refraction.

$$\frac{\sin r}{\sin i} = \frac{n_1}{n_2}$$
(2.5)

When $n_1 > n_2$, $r = 90^o$ at the critical angle of incidence ϕ_c (called Brewster's angle). Upon $i > \phi_c$, the incident ray is total internally reflected. The bending of light rays as they pass from one medium to another is the key to the design of lenses in eyeglasses, microscopes, telescopes, and camera.

The absorption coefficient (α) is defined by Beer-Lambert's law for intensity I transmitted through a distance z of medium:

$$I = I_0 e^{-\alpha z}$$
(2.6)

where I_0 is the incident intensity.
The absorption as due to a solution of the absorbing species in the medium, in which case it is useful to define a molar extinction coefficient δ as

$$a = \delta c$$
(2.7)

Where c is the concentration (mol/L) of the absorb center. δ is expressed as L/mol/cm. The absorbance (A) and the optical density (D) are given by

$$A = -\ln \left[\frac{I}{I_0} \right]$$
(2.8)

$$D = -\log \left[\frac{I}{I_0} \right]$$
(2.9)

Other important criterion in the design of optical components to be considered is the correction for chromatic aberration resulting from the dispersion of light, i.e., the variation of *n* with wavelength. Away from an absorption peak, *n* may be expressed by Cauchy's dispersion formula:

$$n = A' + \frac{B'}{\lambda^2} + \frac{C'}{\lambda^4} + \dots,$$ (2.10)

where *A′*, *B′*, *C′*,… are known as Cauchy coefficients which are characteristic of the material. These coefficients are defined as

$$A' = 1 + \sum_{j=i+1}^{\infty} a_{ij}, \quad B' = 1 + \sum_{j=i+1}^{\infty} a_{ij}\lambda_{ij}^2, \quad C' = 1 + \sum_{j=i+1}^{\infty} a_{ij}\lambda_{ij}^4$$ (2.11)

where $a_{ij} = r_e N f_{ij}\lambda_{ij}^2/2\pi$, $r_e = 2.818 \times 10^{-13}$ cm is the radius of an excited electron experiencing a transition from a lower energy level *i* to a higher energy level *j* when it absorbs a photon associated with a (transition) wavelength λ_{ij}. *N* is the atomic number density. The oscillator strength f_{ij} is a fraction of *N* which takes part in a given *i→j* transition.

For practical purposes, the useful parameters in the correction for chromatic aberration are the Abbe number ν_d and the partial dispersion. The Abbe number is defined by

$$\nu_d = \frac{n_d - 1}{n_F - n_C}$$ (2.12)

where the F-line is the blue $\lambda = 486.1327$ nm line from the hydrogen spectrum, the C-line is red $\lambda = 656.2725$ nm line, also from the hydrogen spectrum, and the d-line is the yellow $\lambda = 587.5618$ nm line from the He spectrum. The partial dispersion for any two wavelengths x and y is given by

$$P_{x,y} = \frac{n_x - n_y}{n_F - n_C}$$ (2.13)

In optical applications of glasses, a map of the variation of refractive index as a function of Abbe number (dispersion) is used. In conventional maps, the designations of the glasses are given as "Crown" and "Flint", which is somewhat confusing. Highly refractive glasses tend to have smaller Abbe numbers, i.e., high relative dispersion. A high refractive index is desirable to increase glass reflectivity (shiny appearance).

The factors affecting refractive-index of the glass are

     1. Polarizability of the first neighbor ions coordinated with it (anion).
     2. Field intensity Z/a^2 (i.e., polarization power), where Z is the valence of the ion (ionic charge) and a is the distance of separation (ionic radius).
     3. Coordination number of the ion.

4. Non-bridging oxygen bonds (NBOs).
5. Electronic polarizability of the oxide ion.
6. Optical basicity of the glasses.

According to Fajan's rules the first two factors mean that to increase electronic polarizability of the material a small positive ion (cation), a large negative ion (anion), and large charges on either ion are required. In the scope of previous factors, the refractive indices behavior of the different glass samples can be analyzed and explained.

2.7 Absorption Processes in Solids [48]

In describing absorption processes in solids, it is possible to categorize the major phenomena under six headings. They are, in order of commonly encountered decreasing energy of the transition:

(1) Electron transitions from the valence band to higher-lying conduction bands, characterized by continuous high-absorption processes with structure variations depending on the density of states distribution in the bands involved. The optical absorption constant is usually in the range 10^5-10^6 cm^{-1}.

(2) Electron transitions form the valence band to the lowest-lying conduction band with a minimum required energy of the forbidden band gap. The magnitude and variation with energy of the absorption constant depends on whether the transition involves a photon only (direct transition) or whether it involves both a photon and a phonon (indirect transition). The absorption constant decreases by many orders of magnitude as the photon energy drops below the band gap energy.

(3) Optical excitation producing a bound electron-hole pair, known as an *exciton*, requiring less energy than to produce a free electron-hole pare by excitation across the band gap. The exciton can be thought of as a hydrogenic system, capable of moving and transporting energy through the crystal without transporting net charge. The electron and hole making up an exciton may be thermally dissociated into free carriers, or may recombine with the emission of light or phonons.

(4) If imperfections are present in the crystal, they create energy levels that lie in the forbidden gap. Therefore at energies less than the band-gap energy it is still possible to excite electrons to the conduction band from imperfection levels occupied by electrons, of to excite electrons from the valence band to unoccupied imperfection levels, each process giving rise to optical absorption. This absorption in turn comes to an end when the photon energy is less than the energy required to make a transition from the imperfection level to one of the bands. For very high imperfection densities, the corresponding absorption constant may have values as high as 10^3 cm^{-1}, but in general is considerably less.

(5) Absorption of photons by free carriers, causing a transition to higher energy states within the same band or to higher bands. This process can occur over a wide range of photon energies. It involves the absorption of both photons and phonons since both energy and *k* must be charged in the transition. There is also an optical absorption due to free carriers action collectively as a kind of "electron gas," which is known as plasma resonance absorption.

(6) Absorption of photons in the excitation of optical mode vibrations of the crystal lattice, known as Reststrahlen absorption. This is the only one of six phenomena that does not involve electronic transitions.

Figure 2.6 illustrates the various electronic absorption process in both flat-band and *E* versus *k* diagram. Note that the *E* versus *k* diagram tell about both changes in *E* and change in *k* during an optical transition, whereas the flat-band diagram can be describe only changes in *E*. In the following section, consider process 2-5 in a little more detail.
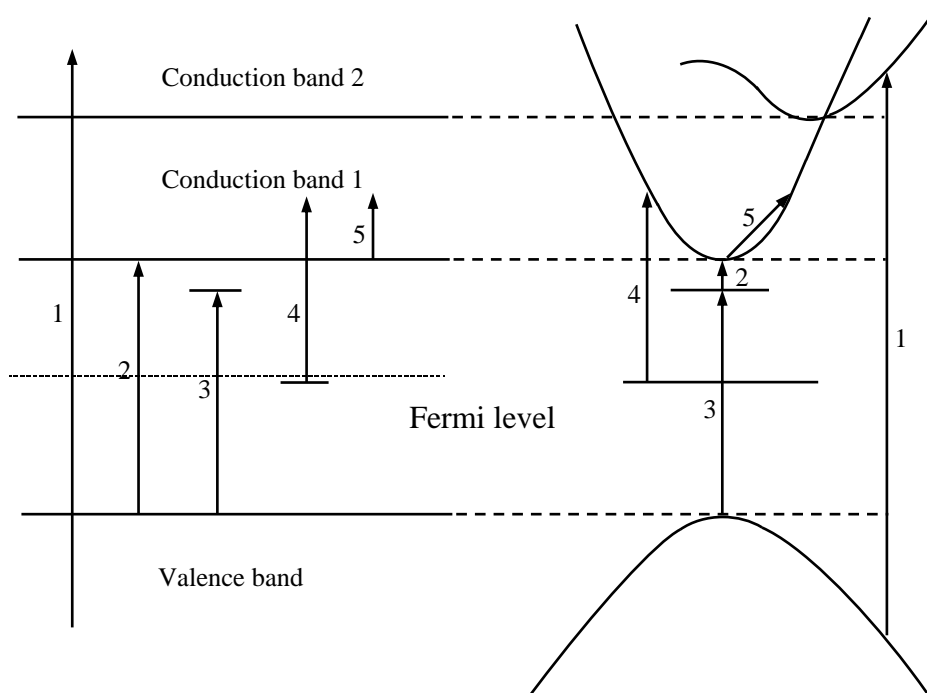

Figure 2.6 Characteristic types of optical transitions shown both for the flat-band model and for the E versus k plot. (1) Excitation from the valence band to higher-lying conduction bands, (2) excitation across the band gap, (3) excitation formation, (4) excitation from imperfections, and (5) free-carrier excitation [32].

2.8 Transitions across the Band Gap [32]

The transition indicated by a (2) on Figure 2.6 are the cause of the fundamental absorption edge of the material, and hence of the apparent color by transmission of many semiconductors and insulators. In speaking of color as perceived by the human eye, the spectral sensitivity curve of the eye must be remembered, with its maximum for the green and lower sensitivity for blue or red. The high reflectivity of metals is caused by free carrier absorption. As the band gap of a semiconductor moves from the ultraviolet to the infrared, the color of the material by transmission changes from colorless to yellow, orange, red, or black, depending on whether all of the visible spectrum or only a portion of the longer wavelength region is being transmitted. Since the band gap absorption process absorbs only higher energy photons, certain colors are not possible for pure semiconductor.

In particular, since a green color by transmission would required absorption of both the blue and rd ends of the spectrum, no semiconductor band gap absorption can give rise to a green colored material by transmission, the only way that a semiconductor could appear green by transmission would be if the band gap absorption removed the blue end of the spectrum and some kind of impurity absorption removed the red end of the spectrum.

Note that color by transmission must be specified, for a material with a band gap in the yellow might appear orange-red by transmission and blue by reflection, since the blue light would be strongly reflected because of its high absorption constant. It should be noted, however, that the subjectively perceived color of most crystalline solids is a result of transmission rather than reflection.

2.9 Evaluation of Absorption Coefficient [32]

Study of the optical absorption edge in UV region has proved to be very useful method for clarification of optical transitions and electronic band structure of the materials.

It is possible to determine indirect and direct transition occurring in band gap by optical absorption spectra at the fundamental absorption edge of the material. In both cases, electromagnetic waves interact with the electrons in the valance band, which are raised across the fundamental gap to the conduction band.

In amorphous materials a different type of optical absorption edge is observed. In these materials, the absorption coefficient (α) increases with the photon energy near the energy gap.

The absorption coefficient α as a function of transmittance T and reflectance R is calculated using the following formula.

$$\alpha = \frac{1}{d} ln \left\{ \frac{(1-R)^2}{2T} + \sqrt{\left[\frac{(1-R)^2}{2T}\right]^2 + R^2} \right\}$$
(2.14)

Where d is denotes the plane parallel sample thickness. The relative error in determination of the absorption coefficient $\Delta\alpha/\alpha$ does not exceed 10%.

The propagation of electromagnetic waves depends on the optical constant of materials, refractive index, n and the extinction coefficient k. Furthermore, n affects the phase of light waves that propagate in the material while k affects its amplitude. The determination of α enables the extinction coefficient k to be obtained from the expression

$$k = \frac{\alpha\lambda}{4\pi}$$
(2.15)

The estimated error δk for the extinction coefficient k is $0.005k$.

According to the strong UV absorption bands, the extinction coefficient k obeys for the different glass samples the Fermi-Dirac distribution function,

$$k(\lambda) = \frac{1}{1 + exp\left[(E_F - E)/k_B T\right]} \tag{2.16}$$

where E_F is Fermi energy. $E = hc/\lambda$ is photon energy. $k_B T$ is represented the thermal energy at an absolute room temperature. h is Planck's constant. k_B is Boltzmann's constant. c is the speed of light in free space.

2.10 Absorption in the UV [34]

Strong absorption bands arising from electron excitations produce essentially a UV cutoff, causing most glasses to appear opaque in the UV. These electron excitations are generally of two types.

1. Intrinsic excitation, where electrons are excited from the valence band to unoccupied states in the exciton or the conduction band (interband transition) levels.

2. Transfer of an electron (charge) between the shells of one ion and the shells of a neighboring ion (interionic transitions). These ions may be major constituents or minor constituents. Electron transfer between neighboring multivalent transition elements, for instance Fe^{2+} to Fe^{3+}, is an example of the latter.

Intrinsic absorption occurs when photon have energies comparable to the band gap E_g. The wavelength of UV cutoff can be estimated by

$$\lambda_c = \frac{hc}{E_g} \tag{2.17}$$

To be more precise, one should replace E_g in this equation by the mobility gap E_0, measure from the valence band mobility edge to the conduction band mobility edge. For photon energies higher than mobility gap, the absorption coefficient α, below and near the edge of each curve was determined at different wavelengths using relation.

$$\alpha = \left(\frac{1}{x}\right) ln\left(\frac{I_0}{I}\right) \tag{2.18}$$

where x is the thickness of the sample, and I_0 and I are the intensity of incident and transmitted radiation, respectively. For the absorption region with $\alpha \geq 10^4$ cm^{-1}, Davis and Mott proposed the relation for the absorption coefficient, $\alpha(v)$, as a function of photon energy (hv) for direct and indirect optical transitions through the following,

$$\alpha(v) = A\frac{(hv - E_g^{opt})^n}{hv} \tag{2.19}$$

where the exponent $n = 1/2$ for allowed direct transition, while $n = 2$ for allowed indirect transition. E_g^{opt} is optical band gap energy and A is a constant related to the extent of the band tailing. It is a temperature independent constant that depends on the refractive index n_0 given by

$$A = \frac{(4\pi/c)\sigma_0}{n_0 \Delta E} \qquad (2.20)$$

where σ_0 is the electrical conductivity. ΔE is the width of the tail of localized states in the normally forbidden gap. Plotting $\alpha h v^{1/2}$ and $\alpha h v^2$ against photon energy $h v$ gives a straight line with intercept equal to the optical energy band gap for indirect E_{g2}^{opt} and direct E_{g1}^{opt} transitions, respectively.

In various glass system, Eq. (2.19) depicts a straight line where $n=2$. The variation of $(\alpha h v)^{1/2}$ with $h v$ (Tauc's plot) is shown in Figure 2.6 for some of the glass samples of the Ba series. The value of Eg for all samples have been calculated by extrapolating the linear region of the curves to meet the $h v$ axis at $(\alpha h v)^{1/2} = 0$.
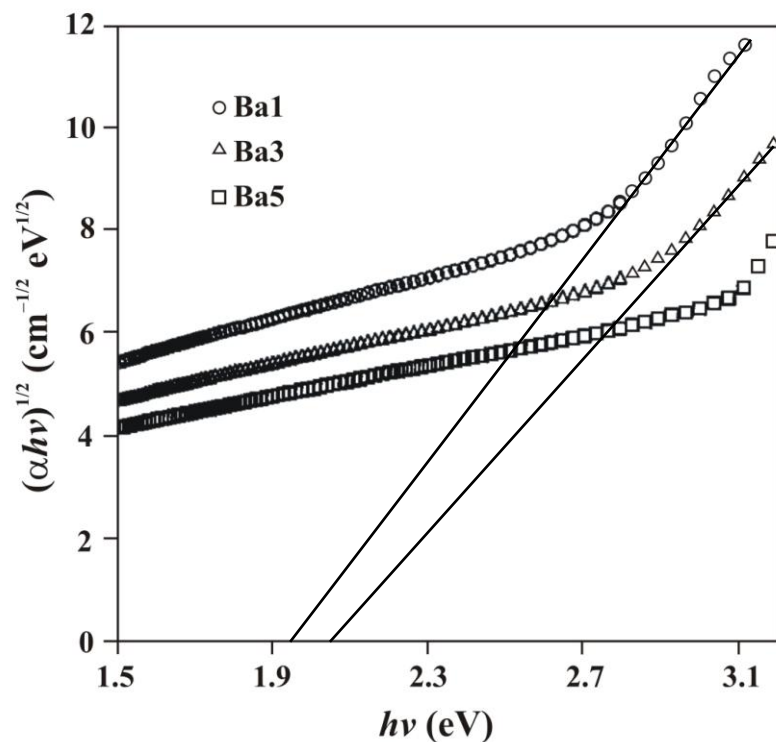

Figure 2.7 Optical absorption edges of $20BaO\text{-}(80\text{-}x)B_2O_3\text{-}xBi_2O_3$ for Ba1 is x=10, Ba3 is x=30, Ba5 is x=50. Extrapolation of the linear regime yields the optical band gap [32].

The main feature of the absorption edge of amorphous materials is an exponential increase of the absorption coefficient with photon energy. When the energy of the incident photon is less than the band gap, the increase in absorption coefficient is followed with an exponential decay of density of states of the localized into the gap.

The absorption edge here is called Urbach edge, where the values are between 10 and 10^3 cm^{-1}. The lack of crystalline long-range order in amorphous/glassy materials is associated with a tailing of density of states into normally forbidden energy.

Urbach energy characterizes the extent of the exponential tail of the absorption edge. The exponential absorption tails and Urbach energy is given in accordance with the empirical relation.

$$\alpha(\nu) = \beta \exp(h\nu / E_U) \tag{2.21}$$

where β is a constant. E_U is the Urbach energy which indicates the width of the band tails of the localized states. ν is the frequency of the radiation. The exponential absorption tails, i.e., Urbach energy depends on temperature, thermal vibrations in the lattice, induced disorder, static disorder, strong ionic bonds, and on average photon energies. The main factor contributing to edge broadening in crystalline materials is exciton phonon coupling (dynamic disorder). In amorphous, an additional broadening due to static disordered exists. The Urbach role has been studies in detail both for crystalline (dynamic disorder) and glassy (static disordered) materials. Figure 2.7 shows the case of the Urbach behavior of $5BaO-15Na_2O-80B_2O_3$ glass system.
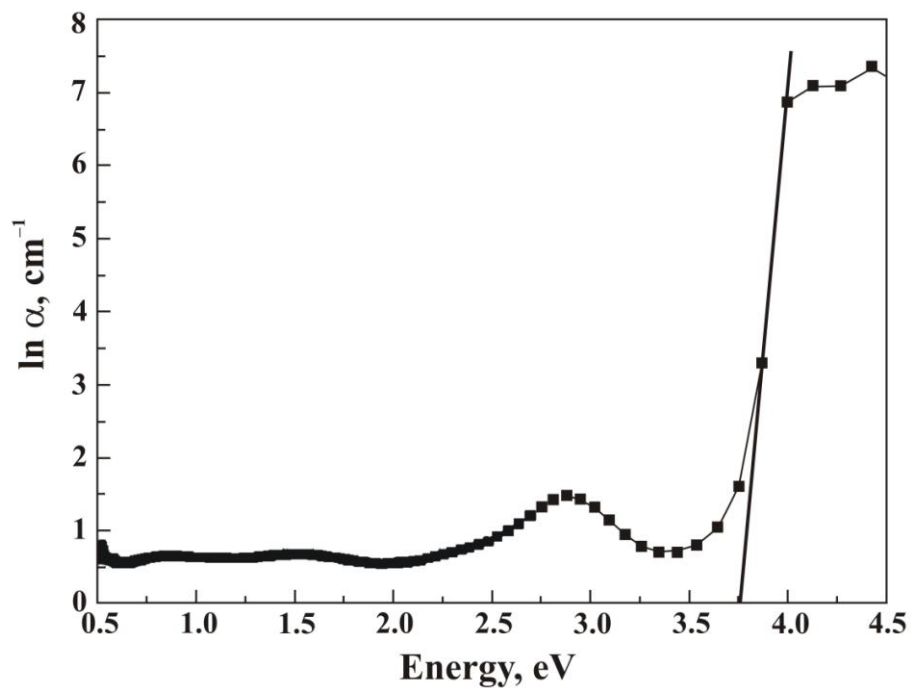

Figure 2.8 Optical absorption edges of $5BaO-15Na_2O-80B_2O_3$ at room temperature, showing Urbach behavior [32].

2.11 Oxygen Ion Activity; Basicity [14]

The chemical interactions between the glass components are of acid-base character. The oxygen atoms in glasses behave as Lewis' bases and they can transfer part of their negative charge to the cations. The ability of oxygen to transfer the negative charges is the greatest when it is situated in the surroundings of weak cations, such as the alkalis. Duffy et al., proposed the concept of optical basicity based on the experimental shift of the ultraviolet spectrum of a probe incorporated in various oxides. Duffy proposed a parameter Λ that permits a comparison of the acid-base character of oxides. The optical basicity Λ, of an oxidic medium, is the average electron donor power of all the oxide atoms comprising the medium. Increasing basicity results in increasing negative charge on the oxygen atoms and, thus, increasing covalence in the cation oxygen bonding.

The optical basicity could be predicted from the glass compositions and from the basicity moderating parameters of the various cations present. It is possible to calculate the so-called theoretical optical basicity of multi-component glass on the basis of the following equation proposed by Duffy and Ingram.

$$\Lambda_{th} = \sum_{i=1}^{n} x_i \Lambda_i \qquad (2.22)$$

where x_1, x_2,..., x_n are equivalent fractions of different oxides, i.e., the amount of oxygen each oxide contributes to the overall glass stoichiometry and Λ_1, Λ_2,..., Λ_n are optical basicity values assigned to the constituent oxides.

Since the polarizability of oxide ions is closely related to the optical basicity of oxide materials, the studied glasses possess a relatively low optical basicity with the increase in the value of x. This may be understood according to the relation.

$$\Lambda_{th} = 1.67\left(1 - \frac{1}{\alpha_0^{2-}}\right) \qquad (2.23)$$

where α_0^{2-} is polarizability of oxide ions. The equation (2.23) shows that decreasing polarizability, the optical basicity decreases leading to decrease to refractive index. Theoretical values of optical basicity, electronic polarizabilities, and related parameters for calculated of bismuth borate glass are listed in Table 2.1 and 2.2.

Table 2.1 Optical basicities according to Dimitrov and Sakka calculated from refractive index ($\Lambda(n_0)$) and energy gap ($\Lambda(E_g)$), their average (Λ_{av}), optical basicity according to Duffy (Λ_{Duffy}), optical basicity according to Lebouteiller and Courtine (Λ_{LS}), and binding energy (E_b) of simple oxides [14].

Oxides	$\Lambda(n_0)$	$\Lambda(E_g)$	Λ_{av}	$\Lambda_{(Duffy)}$	Λ_{LS}	E_b (eV)
Bi_2O_3		1.190	1.190		1.190	
B_2O_3	0.430		0.430	0.420	0.420	533.20
Dy_2O_3	0.945	1.291				

Table 2.2   Electronic polarizabilities of oxide ion calculated from refractive index (α_0^{2-} (n_0)) and energy gap (α_0^{2-} (E_g)), average ($^{av}\alpha_0^{2-}$), and O1**s** binding energy (E_b) of simple oxides [14].

Oxides	α_0^{2-} (n_0) (A^3)	α_0^{2-} (E_g))(A^3)	$^{av}\alpha_0^{2-}$ (A^3)	E_b (eV)
Bi_2O_3		3.507	3.507	
B_2O_3	1.345		1.345	533.20
Dy_2O_3	2.303	4.401		

2.12 Luminescence [34]

Luminescence or emission of light by certain materials is often called cold light. Luminescence emission occurs after an appropriate material has absorbed energy from a source such as ultraviolet, x-ray radiation, electron beams, proton beams, and so on. The energy lifts the atoms of the material into an excited state, and then, because excited states are unstable, the material undergoes another transition, back to its unexcited ground state, and the absorbed energy is liberated in the form of either light or heat or both (all discrete energy states, including the ground state, of an atom are defined as quantum states). The excitation involves only the outermost electrons orbiting around the nuclei of the atoms. Luminescence efficiency depends on the degree of transformation of excitation energy into light, and there are relatively few materials that have sufficient luminescence efficiency to be of practical value. Luminescence is characterized by electrons undergoing transitions from excited quantum states. The excitation of the luminescent electrons is not connected with appreciable agitations of the atoms that the electrons belong to.

Photoluminescence, which occurs by virtue of electromagnetic radiation falling on matter, may range from visible light through ultraviolet, x-ray, and gamma radiation. It has been shown that, in luminescence caused by light, the wavelength of emitted light generally is equal to or longer than that of the exciting light (i.e., of equal or less energy). As explained below, this difference in wavelength is caused by a transformation of the exciting light, to a greater or lesser extent, to nonradiating vibration energy of atoms or ions. In rare instances e.g., when intense irradiation by laser beams is used or when sufficient thermal energy contributes to the electron excitation process. The emitted light can be of shorter wavelength than the exciting light (anti-Stokes radiation).

The fact that photoluminescence can also be excited by ultraviolet radiation was first observed by a German physicist, Johann Wilhelm Ritter (1801), who investigated the behavior of phosphors in light of various colors. He found that phosphors luminescence brightly in the invisible region beyond violet and thus discovered ultraviolet radiation. The transformation of ultraviolet light to visible light has much practical importance.

Gamma rays and x-rays excite crystal phosphors, glasses, and other materials to luminescence by the ionization process (i.e., the detachment of electrons from atoms), followed by a recombination of electrons and ions to produce visible light. Advantage

of this is taken in the fluoroscope used in x-ray diagnostics and in the scintillation counter that detects and measures gamma rays directed onto a phosphor disk that is in optical contact with the face of a photomultiplier tube (a device that amplifies light signals).

2.13 Mechanism of Luminescence [34]

The emission of visible light corresponding to the region between deep red and deep violet) requires excitation energies the minimum of which is given by Einstein's law stating that the energy (E) is equal to Planck's constant (h) times the frequency of light (ν), or Planck's constant times the velocity of light (c) in a vacuum divided by its wavelength (λ); that is,

$$E = h\nu = \frac{hc}{\lambda} \qquad (2.24)$$

The energy required for excitation therefore ranges between 40 kcal (for red light), about 60 kcal (for yellow light), and about 80 kcal (for violet light) per mole of substance. Instead of expressing these energies in kilocalories, electron volt units (1 eV = 1.6×10^{-19} J = 1.6×10^{-12} erg; the erg is an extremely small unit of energy) may be used, and the photon energy thus required in the visible region ranges from 1.8 eV to 3.1 eV.

The excitation energy is transferred to the electrons responsible for luminescence, which jump from their ground state energy level to a level of higher energy. The energy levels that electrons can assume are specified by quantum mechanical laws. The different excitation mechanisms considered below depend on whether or not the excitation of electrons occurs in single atoms, in single molecules, in combinations of molecules, in glasses, or in a crystal. They are initiated by the means of excitation described above: impact of accelerated particles such as electrons, positive ions, or photons. Often, the excitation energies are considerably higher than those necessary to lift electrons to a radiative level. The color of the luminescent light is nearly independent of the energy of the exciting particles, depending chiefly on the excited state energy level of the crystal centre.

Electrons taking part in the luminescence process are the outermost electrons of atoms or molecules. In fluorescent lamps, for example, a mercury atom is excited by the impact of an electron having an energy of 6.7 eV or more, raising one of the two outermost electrons of the mercury atom in the ground state to a higher level. Upon the electron's return to the ground state, an energy difference is emitted as ultraviolet light of a wavelength of 185 nm. A radiative transition between another excited state and the ground state level of the mercury atom produces the important ultraviolet emission of 254 nm wavelength, which, in turn, can excite other phosphors to emit visible light. (One such phosphor frequently used is a calcium halophosphate incorporating a heavy metal activator.) This 254 nm mercury radiation is particularly intensive at low mercury vapour pressures (around 10^{-5} atm) used in low pressure discharge lamps. About 60 percent of the input electron energy may thus be transformed into near monochromatic ultraviolet light i.e., ultraviolet light of practically one single wavelength.

Whereas at low pressure there are relatively few collisions of mercury atoms with each other, the collision frequency increases enormously if mercury gas is excited under high pressure (e.g., 8 atm or more). Such excitation leads not only to collisional de-excitation of excited atoms but also to additional excitation of excited atoms. As a consequence, the spectrum of the emitted radiation no longer consists of practically one single, sharp spectral line at 254 nm, but the radiation energy is distributed over various broadened spectral lines corresponding to different electronic energy levels of the mercury atom, the strongest emissions lying at 303, 313, 334, 366, 405, 436, 546, and 578 nm. High pressure mercury lamps can be used for illumination purposes because the emissions from 405 to 546 nm are visible light of bluish green color; by transforming a part of the mercury line emission to red light by means of a phosphor, white light is obtained.

The terms fluorescence and phosphorescence can be used here, on the basis not only of the persistence of luminescence but also of the way in which the luminescence is produced. When an electron is excited to what is called, in spectroscopy, an excited singlet state, the state will have a lifetime of about 10^{-8} sec, from which the excited electron can easily return to its ground state (which normally is a singlet state, too), emitting its excitation energy as fluorescence. During this electronic transition the spin of the electron is not altered; the singlet ground state and the excited singlet state have like multiplicity (number of subdivisions into which a level can be split). An electron, however, may also be lifted, under reversal of its spin, to a higher energy level, called an excited triplet state. Singlet ground states and excited triplet states are levels of different multiplicity. For quantum mechanical reasons, transitions from triplet states to singlet states are "forbidden," and, therefore, the lifetime of triplet states is considerably longer than that of singlet states. This means that luminescence originating in triplet states has a far longer duration than that originating in singlet states: phosphorescence is observed.

The interactions of a large number of atoms, ions, or molecules are greater still in solution and in solids; to obtain a narrowing of the spectral band, subzero temperatures (down to that of liquid helium) are applied in order to reduce vibrational motions. The electronic energy levels of crystals such as zinc sulfide and other host crystals or glasses used in phosphors form bands: in the ground state practically all electrons are to be found on the valence band, whereas they reach the conduction band after sufficient excitation. The energy difference between the valence band and the conduction band corresponds to photons in the ultraviolet or still shorter wavelength region. Additional energy levels are introduced by activator ions or centers bridging the energy gap between valence band and conduction band, and, when an electron is transferred from the valence band to such an additional energy level by excitation energy, it can produce visible light on return to the ground state. A rather close analogy exists between the forbidden transitions of certain excited molecular electronic states (triplet–singlet, leading to phosphorescence) and the transition of an electron of an inorganic phosphor kept in a trap: traps (certain distortions in the crystal lattice) are places in the crystal lattice where the energy level is lower than that of the conduction band, and from which the direct return of an electron to the ground state is also forbidden.

2.14 The Phenomenon of Scintillation [47]

Scintillation properties have played a major role in the development of physics and material sciences. Scintillation materials are ideal devices to detect elementary particles

and to measure their parameters. Scintillation can be observed in various organic and inorganic crystalline media and glasses, as well as in fluids, and gases.

Kallmann, H. (1949) defined scintillation as flash of light in phosphorus. Physics Encyclopedia Big Russian Encyclopedia, scintillation defined as "the short light flashes originating in a scintillator under the effect of ionizing radiation". Fünfer, E. and Neuert, H. (1959) defined scintillation as "the phenomenon of luminescence in transparent solids, fluids, or gases, originating the propagation of the ionizing radiation through them".

There are three fundamental mechanisms of electromagnetic interactions when traversing a medium:

  (a) photoabsorption,
  (b) Compton scattering, and
  (c) electron-positron pair formation.

Scintillation can be defined as a wavelength shifter. It converts the energy (or wavelength) of an incident particles or energetic photon (UV, x-ray, or gamma-ray) into a number of photons of much lower energy (or longer wavelength) in the visible or near visible range, which can be detected with photomultipliers, photodiodes, avalanche photodiodes, or spectrophotometers. Scintillation occurs as the result of a chain of process, which are characterized by different time constants, taking into account the existence of thresholds of "hot" electrons and holes inelastic interaction. Four essential phases are distinguished and listed in Table 2.3.

Table 2.3 The sequence of processes leading to scintillation in a medium [47].

Phase	Characteristic Time, s
1 *Energy conversion*: Initial energy release with formation of "hot" electrons and holes	$\tau_1 = 10^{-18} - 10^{-9}$
2 *Thermalization*: Inelastic processes of interaction of "hot" electrons and holes and their thermalization.	$\tau_2 = 10^{-16} - 10^{-12}$
3 *Transfer to luminescent centers*: Formation of excitonic states and groups of excited luminescent centers.	$\tau_3 = 10^{-12} - 10^{-8}$
4 *Light emission*: Relaxation of excited luminescent centers and emission of scintillation light.	$\tau_4 > 10^{-10}$

The initial energy release in a medium occurs in a wide time range; however, its duration cannot be smaller than $2R/c$, where $R \approx 10^{-10}$ m is the order of atomic radius and c is the light speed. It also cannot exceed the transit time of particle or $\gamma -$ quantum in the scintillator and, for crystalline inorganic compounds, is restricted to a few nanoseconds. It must be noticed at this stage that the transfer to the detecting medium of at least a fraction of the energy of a particles does not necessarily require the transit of that particle through the medium. The transverse electrical field associated with a relativistic particle traveling close to the surface of a dielectric inorganic scintillator can

in fact penetrate the medium and therefore interact with the electrostatic field of the crystal. This phenomena could be exploited for the monitoring of intense particles beams near a flat surface or through nanotubes.

The "hot" electrons and holes inelastic scattering process and their thermalization are rather fast in heavy crystals generally used as scintillating materials which are characterized by a high density of electronic states.

The formation of excitonic state and the transfer of their excitation to luminescent centers occur with characteristic time constants which are generally in the picosecond range.

At the end of the process the relaxation of the excited luminescent centers and the corresponding light emission is characterized by time constants distributed in a wide time range which are determined by the quantum wave function characteristics of the different levels involved in the transitions.

It must be noticed here that the excitation of the scintillation by a charge particle does not necessarily require direct impact of the particle with the electrons and nuclei of the scintillation medium. Energy is transferred from the particle to the scintillation through the electromagnetic field associated to the particle. It is therefore possible to excite the luminescence of scintillator by a relativistic particle (the transverse extension of the electromagnetic wave is larger in this case) traveling very close to its surface without penetrating it.

Therefore, *scintillation* is the luminescence induced by ionizing radiation in transparent, dielectric media.

This complex sequence of phenomena characterizes the scintillation process, contrary to the photoluminescence which results from the direct excitation of the luminescent centers.

The kinetics is therefore more complex in many cases, contrary to what can be observed in gases, condensed gases, fluids, and their vapors. In such media the atoms of the gas or molecules of organic dyes or anionic complexes of rare-earth ions can be considered to some extent as free with almost no interaction with other particles of the medium. The luminescence decay time is therefore equal to the radiating decay time τ_r of luminescent centers excited states. It means that all the light quanta have been emitted after a few τ_r. On the other hand, crystalline compounds are characterized by a noncontinuous electronic energy distribution with an energy gap $E_g >> kT$, separating a filled valence electronic band from higher energy and generally not populated levels forming the conduction band. The width of the forbidden band between the valence and the conduction band determines if the material is a semiconductor (2-3 eV) or an insulator (> 3 eV, typically ≥ 4 eV).

For a given material, a plurality of luminescent centers, whose radiating levels are localized in the forbidden zone, can coexist and interfere with each other. Some of these luminescent centers are cations or anionic complexes of the lattice or doping ions such as Dy^{3+} specifically introduced at the crystal growth. Some others are generated by the

interaction of the ionizing radiation with the medium. Such induced centers play an important role in the scintillation as they can sensitize or quench luminescence or act as electron or hole donors for existing radiating centers via a secondary excitation process. In practice this secondary excitation is generated not only by direct Coulomb interaction but also by thermoactivation or electron tunneling from matrix host defects with trap electrical carriers produced by the incident particle. The kinetics of primary and secondary excitation processes are different. If we define ω_{int} as the frequency of interaction between primary and secondary luminescent centers in the medium, we can distinguish different cases, depending on how the mean time between interactions compares with the time of information of primary excited luminescent centers τ_3 and with their radiating decay time τ_r.

For

$$1/\omega_{int} \approx \tau_3 << \tau_r \tag{2.25}$$

e kinetics of the direct scintillation will dominate, characterized by a very fast rise time followed by a single exponential decay, the signature of the radiative relaxation of the luminescent center.

If on the other hand

$$1/\omega_{int} >> \tau_r \quad \text{and} \quad 1/\omega_{int} >> \tau_3 \tag{2.26}$$

wich is frequently the case in real materials, the direct scintillation is accompanied by a phosphorescence which results from the delayed decay of the secondary luminescent centers. The interaction of luminescent centers between themselves or with charge carriers traps leads to the more complex kinetics with generally longer rise time and strong nonexponential decay with long tails in some cases. As a measure of the contribution of phosphorescence in scintillation, the afterglow parameter is used. *Afterglow* is the amplitude of the luminescence signal, excited by ionizing radiation and measure after a fixed time.

Scintillation is characterized by several parameters. Some of them depend on the shape, surface state, and optical quality of the scintillator block. This research was to study and characterize the luminescence and scintillation properties of dysprosium (Dy^{3+} ions) doped in bismuth borate glasses.

2.15 Rare-Earth Ions in Glasses [34]

Rare-earth atoms are divided in to two classes. The first one is lanthanides with atomic number 57 through 71 and the second is actinides with atomic number 89 through 103. Rare-earth (RE) ions (4f electronic configuration) doped glasses have been studied and applied for several years in a variety of applications. On dissolution in glass, the majority of the rare-earth ions introduce very sharp and distinctive absorption bands into the spectral transmission curve. The absorption spectra are due to electronic transitions between energy levels in the *4f* shell. Their sharpness is due to the fact that the inner electronic shell is largely shielded from the effects of the ligand field by the outer *5s* and *5p* electrons. The ligand field is, basically, a perturbation on the energy

levels, introducing fine structure to the absorption spectra. In contrast the ligand field for transition metal ions in glass is a factor of a hundred stronger and the absorption spectra are due to transitions between levels produced directly by the field.

Though sharp, the intensities of the absorption bands are relatively weak, the optical absorption coefficients being a factor of ten lower than for the transition ions. Judd has accounted for such intensities by assuming that transitions of electric dipole character originate from the admixture of terms of opposite parity with the *4f* wave functions.

The complexity of the glass absorption spectra depends on the number of unpaired electrons in the *4f* shell. The spectra of cerium, europium, gadolinium, ytterbium and lutetium (Lu)X are relatively simple, reflecting the stability of the empty, half full and filled *5f* electronic shell. In contrast praseodymium, neodymium, terbium, dysprosium, holmium, erbium and thulium impart an array of sharp absorption bands, extending from the near infrared through to the ultraviolet region.

The rare-earth elements do not occur separately in nature, but as mixtures, in such ores as monazite, a rare-earth thorium phosphate. The relative abundance of each element as a commercial product is in proportion to its concentration in such ores. Dysprosium was occurs along with other so-called rare-earth or lanthanide element groups in a variety of minerals such as xenotime, fergusonite, gadolinite, euxenite, polycrase, and blomstrandine. The most important sources are from monaziate and bastnasite. The chemical similarity of the elements makes the ore extraction procedures for their separation highly complex and costly. Rare-earth oxides are therefore relatively expensive as coloring agents. Furthermore, because of their low absorption coefficients, relatively high colorant concentrations are required. As a consequence their utilization is limited and mainly confined to optical and ophthalmic glass, and to high quality decorative ware. The aim of this research was to study and characterize the properties of dysprosium doped in bismuth borate glasses. Some specific properties of luminescence wavelength and transition levels of dysprosium were showed as Table 2.3.

Table 2.4 Luminescence wavelengths and transition levels of tri-valence of rare-earth ions (dysprosium, Dy^{3+}) doped in bismuth borate glasses.

Rare-earth ions	Electron configurations	Luminescence wavelengths (mm)	Color Bands	Transition levels
Dy^{3+} Ground state $^6H_{15/2}$	$1s^2\ 2s^2\ 2p^6\ 3s^2$ $3p^6\ 4s^2\ 3d^{10}\ 4p^6$ $5s^2\ 4d^{10}\ 5p^6\ 6s^2$ $4f^{10}$	660 575 480	Red Yellow Blue	$^4F_{9/2} \rightarrow {}^6H_{11/2}$ $^4F_{9/2} \rightarrow {}^6H_{13/2}$ $^4F_{9/2} \rightarrow {}^6H_{15/2}$